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ABSTRACT

This paper presents a comparison of experimental results from the analysis of drinking water before and after water treatment using 1 million gallon per day (mgpd) granular activated carbon (GAC) contactors at the Cincinnati Water Works. The following methods of organic analysis were used:

1) Grob closed-loop stripping analysis (CLSA) using capillary GC/MS/DS.

2) Bellar purge and trap (P&T) using packed column GC/Hall/DS, ie, EPA Method 601.

3) Batch Liquid - Liquid Extraction (BLLE) using capillary GC/-MS/DS, and

4) XAD-2 adsorption - ethyl ether elution (XAD-EEE) capillary GC/MS/DS.

At least twice as many "consent decree" organics (23) and the "EPA Office of Drinking Water chemical indicators of industrial contamination" (18) were measured by Grob CLSA than by Bellar P&T, BLLE, and XAD-EEE analyses. Furthermore, Grob CLSA produced this superior analysis at a low cost-per-compound-analyzed figure. Of the 183 different organics which were measured by the four methods, six organics were detected by Bellar P&T, 107 by Grob CLSA, 90 by BLLE, and 58 by XAD-EEE analysis. A historical review of Grob CLSA is presented, as well as a brief review of current U.S. P&T methods. The design of a superior analytical scheme for the comprehensive analyses of purgeable organics in drinking water is indicated by the data. The combined use of Bellar P&T (EPA Methods 601 or 502), Grob CLSA, and BLLE analyses provides useful data on the level of many EPA regulated organics in drinking water.

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16. ABSTRACT
This paper presents a comparison of experimental results from the analysis of drinking water before and after water treatment using 1 million gallon per day (mgpd) granular activated carbon (GAC) contactors at the Cincinnati Water Works. The following methods of organic analysis were used: 1) Grob closed-loop stripping analysis (CLSA) using capillary GC/MS/DS, 2) Bellar purge and trap (P&T) using packed column GC/Hall/DS, ie, EPA Method 601, 3) Batch Liquid - Liquid Extraction (BLLE) using capillary GC/MS/DS, and 4) XAD-2 adsorption - ethyl ether elution (XAD-EEE) capillary GC/MS/DS. At least twice as many "consent decree" organics (23) and the "EPA Office of Drinking Water chemical indicators of industrial contamination" (18) were measured by Grob CLSA than by Bellar P&T, BLLE, and XAD-EEE analyses. Furthermore, Grob CLSA produced this superior analysis at a low cost-per-compound-analyzed figure. Of the 183 different organics which were measured by the four methods, six organics were detected by Bellar P&T, 107 by Grob CLSA, 90 by BLLE, and 58 by XAD-EEE analysis. A histroical review of Grob CLSA is presented, as well as a brief review of current U.S. P&T methods. The design of a superior analytical scheme for the comprehensive analysis of purgeable organics in drinking water is indicated by the data. The combined use of Bellar P&T (EPA Methods 601 or 502), Grob CLSA, and BLLE analyses provides useful data on the level of many EPA regulated organics in drinking water.

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The Exposure Evaluation Branch of the Health Effects Research Laboratory, Cincinnati, Ohio, (HERL-CI) is responsible for validating sensitive and reproducible organic analysis procedures which are used in our research to determine the health effects of chemical contaminants of drinking water. The data presented were obtained in January 1980, when HERL-CI was evaluating different procedures (lyophilization, reverse osmosis, and XAD-2 adsorption) for concentrating organics in drinking water. The resulting concentrated organics are used by HERL-CI for biological toxicity testing. XAD-2 resin was used in this situation to concentrate organics for biological testing purposes and not as an analytical procedure.

Since there continues to be a great deal of interest among environmental chemists concerning the comprehensive analysis of purgeable organics in drinking water, we decided to present at this symposium some of our January 1980, Grob CLSA data and compare it with data from several more conventional

Reference: Melton, R.G., W.E. Coleman, R.W. Slater, F.C. Kopfler, W.K. Allen, T. A. Aurand, D.E. Mitchell, S.J. Voto, S.V. Lucas, and S.C. Watson, "Comparison of Grob Closed-Loop-Stripping Analysis (CLSA) to Other Trace Organic Methods", Advances in the Identification and Analysis of Organic Pollutants in Water, II, (L.H. Keith, ed.), Ann Arbor Sci. Pub. Inc., Ann Arbor, MI. (1981).

methods of organics analysis. For researchers studying the health effects and use of alternate disinfectants, such as chlorine dioxide, chloramines, and ozone, or the use of granular activated carbon in the treatment of drinking water, simple packed-column gas-chromatographic/flame ionization detector (GC/FID) chromatograms of organic components over 100 ng/l in concentration do not provide data upon which decisions can be based. Instead, state-of-the-art methods that use internal standards (IS) spiked in water samples, a high degree of organic concentration, high resolution capillary column separations, reproducible gas chromatography/mass spectrometry (GC/MS) measurements, and sophisticated computerized quantification methods are required.

Since the presentation of our papers[1,2] in Mexico City at this same symposium five years ago on the Bellar purge and trap (P&T) gas chromatography/mass spectrometry/data system (GC/MS/DS) analysis of drinking water, we have followed with great interest new developments in the methodology of purgeable organic analysis. Even though chemists worldwide have learned a great deal in the past five years about comprehensive analysis of volatile organics in water, there is no consensus at this time as to the optimum method or methods of comprehensive analysis of purgeable organics in drinking water. For example, the literature indicates that most European environmental chemists would recommend Grob CLSA (a P&T Method) with wall-coated open tubular (WCOT) capillary GC/MS as the best method, whereas, most environmental chemists in North America would probably recommend some alternative method. We became interested in applying comprehensive capillary GC/MS/DS methodology to our health effects research objectives soon after the development of the CLSA method by Grob in 1973. Progress in using Grob CLSA was slow in our laboratory between 1975 and 1977 until WCOT capillary column techniques were learned. In the past two years we have measured approximately 500 unique purgeable organics using

Grob capillary GC/MS/DS CLSA. We published a preliminary report[3] in December, 1979, detailing some of our CLSA results and applications. The present report reviews briefly U.S. P&T Methods and presents some comparative analytical data of surface water samples (Cincinnati tap water before and after granular activated carbon [GAC] treatment) using the following four methods of analyses:

Method A	Bellar Purge and Trap Analysis (EPA Method 601)
Method B	Grob Capillary GC/MS/DS CLSA
Method C	Batch Liquid-Liquid Extraction (BLLE) Analysis Using a Modified Master Analytical Scheme (MAS) Procedure
Method D	XAD-2 Adsorption - Ethyl Ether Elution Method (XAD-EEE)

The authors wish to clearly point out at the outset that even though the subsequent data indicates the presence of many organics in water from the Cincinnati Waterworks (CWW), these specific Cincinnati drinking water samples are less contaminated than most tap water samples that we have analyzed from other locations. For example, the average concentration of Grob CLSA purgeable organics (other than trihalomethanes) in water samples from CWW was 9.2 ng/l. Grob capillary GC/MS/DS CLSA is an extremely sensitive method of trace organic analysis. In fact, the lower GC/MS detection limit of Grob CLSA for over 200 organics is 1 to 10 ng/l. Therefore, the reader should bear in mind that very reproducible chemical data of trace levels of volatile organics in relatively "clean" drinking water samples is being presented. Secondly, not all laboratories require purgeable organic analytical methods that are as sensitive and comprehensive as Grob CLSA. Certainly, research laboratories that are generating chemical data on which important decisions concerning the choice of drinking water treatment processes, such as research on the use of

granular activated carbon (GAC), alternate disinfectants, filtration techniques, and the health effects of such water treatment processes should use state-of-the-art comprehensive analytical methods such as those which are proposed in EPA's Master Analytical Scheme[4-10]. However, most laboratories are not equipped with good state-of-the-art capillary GC/MS/DS hardware and software, and the capital investment of comprehensive capillary GC/MS/DS methods should be put in perspective with the required objectives of each laboratory. Environmental scientists also realize that the cost per organic compound analyzed is constantly decreasing due to major improvements in analytical methods and laboratory hardware and software. Five years ago[2] we identified the presence of 60 purgeable organics in Miami tap water using an "exotic" instrument (GC/MS) and the Bellar P&T method. Today, this same analysis (EPA Method 624) is no longer considered "exotic". In fact, it is now being used by several U.S. waterworks laboratories. Perhaps five years from now, Grob capillary GC/MS/DS CLSA and other comprehensive trace organic procedures will be "affordable" to more environmental and drinking water laboratories. The Grob CLSA data for 292 organics in this paper were produced by our laboratory group and further illustrate the application of Grob CLSA in drinking water treatment research and in the determination of the health effects of drinking water treatment processes.

In a second chapter[11] of this text, W. Emile Coleman of our group, presents a discussion of the use of GC/MS/DS and internal standards for long-term quantification studies. In a third chapter[12], Jack DeMarco et al. of the Municipal Environmental Research Laboratory of U.S. EPA, will present chemical data obtained over a four-month period on the effect of full scale GAC contactors (one million gallon per day [mgpd]) at the Cincinnati Waterworks. The Grob CLSA results presented by DeMarco et al. were conducted by the Exposure Evaluation Branch of HERL-CI.

HISTORICAL BACKGROUND OF GROB CLSA

In 1973 in Zurich, Switzerland, Grob[13] reported on CLSA for the measurement of purgeable, intermediate molecular weight organics in drinking water at the part-per-trillion (nanogram-per-liter) level. Later, in 1974, Bellar[14,15] reported his P&T method for the analysis of purgeable volatile organics at the part-per-billion (microgram-per-liter) level. U.S. water analysis laboratories quickly adopted the Bellar P&T method[1,2,16] using packed GC columns, whereas Western European laboratories adopted the Grob CLSA method which uses WCOT capillary columns. The primary reason for slow adoption of the Grob CLSA in the U.S. was the slow acceptance of state-of-the-art WCOT glass capillary column technology and capillary column hardware by U.S. manufacturers. Presently, U.S. laboratories remain behind our Western European counterparts in the use of capillary GC for the separation of environmental pollutants. Comprehensive organic analytical procedures, such as Grob CLSA and GC procedures in the Master Analytical Scheme (MAS), require the use of high resolution capillary column separations. Fortunately, U.S. manufacturers and environmental laboratories are beginning to catch up with our Western European counterparts. For this reason, the use of comprehensive trace organic methods in the U.S. can now realistically be proposed.

Grob CLSA utilizes 1.5 mg of activated carbon as a trapping adsorbent[17]. Activated carbon has been used in the past to monitor organic pollutants in air. For example, White et al. of the National Institute for Occupational Safety and Health (NIOSH), reported[18] a standard method in 1970 to measure selected solvent vapors in industrial atmospheres. The NIOSH method involves passing a standard 10-liter volume of industrial room air through a standardized adsorption tube that is packed with activated carbon. After capping the tube and shipping it back to the laboratory, the activated carbon is removed from the tube and placed in a clean vial. One ml of carbon disulfide (CS_2) is added, and the resulting

solution analyzed by GC/FID. All phases of this method have been standardized, and the equipment is readily available.

Grob has thoroughly discussed the design and development of the CLSA procedure in his first CLSA paper[13]. Like the NIOSH air analysis method[18], Grob uses CS_2 to elute the organics from the activated carbon and gas chromatography to separate the organics in the eluant. Like the Bellar P&T method[14], the CLSA method is a vapor-phase P&T stripping technique in which those compounds with appreciable vapor pressure over water are removed from the sample by purging it with a large volume of gas and by passing the stripping gas through an adsorption tube. Unlike other vapor phase procedures, Grob has achieved nearly a one millionfold concentration of most low and intermediate molecular weight organics by using a closed loop design where 0.5 liters of stripping gas is recycled continuously through the water sample, and the adsorption trap is extracted with 12 ul of CS_2. Quantitation is achieved by spiking the initial water sample with a series of internal standards and reference standards, by stripping at 30°C for two hours, and by chromatographing the CS_2 extract on a WCOT capillary column. Grob reported the capillary GC/MS identification of 62 organics in samples of Lake Zurich water and Zurich potable water (ca. 60% comes from Lake Zurich) in this initial CLSA paper.

Grob's second paper[19] on CLSA was dedicated primarily to the application of CLSA to raw and finished drinking water in the area of Zurich. Using capillary GC/MS for identification, K. Grob and G. Grob reported the occurrence of 136 organics in area water at the low ng/l range and demonstrated that automobile gasoline was the major pollutant in Lake Zurich. In these first two CLSA papers[13,19] Grob identified 29 unique alkanes and 34 alkyl-substituted benzenes in Zurich raw and finished drinking water.

In 1975, K. Grob, K. Grob, Jr., and G. Grob[20] compared CLSA with a new trace organic analysis technique, rapid liquid extraction. Grob points out the complementary nature of the two procedures. CLSA is very sensitive for low and intermediate molecular weight nonpolar organics, whereas, rapid solvent extraction is the method of choice for heavier compounds. He also points out something that many environmental laboratories have recently rediscovered; Solvent extracts of water heavily stress capillary GC columns, because nonvolatile components in the extracts shorten column life. In contrast, CLSA extracts contain GC volatile substances so that capillary columns may be used over a very long period of time without any loss of column performance.

In 1976, Grob and Zurcher[17] improved and standardized the CLSA procedure when they realized that many water research laboratories (mostly European) were already using the procedure routinely to study source pollution and drinking water treatment techniques, such as the use of bank filtration, activated carbon adsorption, and alternate disinfection. Grob, as he has in previous papers, clearly points out the major limitations of CLSA, such as the limited intermediate volatility and molecular weight range of substances that are readily measured by the method. Most laboratories that are using CLSA to measure low level organics in water are following this standardized method and have made only slight modifications of it.

We have recorded a total of 16 additional references from seven different laboratories (five European) that have used Grob CLSA to measure 192 unique organics in water. However, a brief tour of European drinking water laboratories will indicate that CLSA is being used daily in many waterworks. Stieglitz *et al.*[21] in West Germany published in 1976 an early comprehensive applications paper. They used capillary GC/MS CLSA exclusively to measure 103 organics at three different water utilities on the Rhine River. Their data clearly show

some of the effects on the raw water of different treatment techniques, such as bank filtration, chlorination, and ozonation. Stieglitz modified the CLSA method of Grob and Zurcher in order to analyze water from the heavily contaminated Rhine River. Two-liter samples were stripped at pH 3 in two different stages.After 15 minutes of stripping, the first activated carbon filter was removed from the loop and a new filter inserted. Stripping was then continued for an additional two hours and 45 minutes. Each filter was extracted separately, and the eluants of filters I and II were combined prior to capillary GC/MS analysis. Stieglitz reported a relative standard deviation of 10 to 15% for 24 organics at the 100 ng/l level, and an average GC/MS detection limit of 0.2 ng/l.

Starting in 1976, Giger in Dubendorf, Switzerland, began publishing the following series of comprehensive application papers using Grob CLSA. Zurcher and Giger[22] reported the occurrence of 70 organics at different points on the Glatt River using capillary GC/MS. Giger, Reinhard, Schaffner, and Zurcher[23] reported in Mexico City five years ago the capillary GC/MS analysis of trace organics using methylene chloride solvent extraction and Grob CLSA. In 1978, Giger, Molnar, and Wakeham[24] applied Grob CLSA to trace the source of chlorinated volatile hydrocarbons in groundwaters and lake waters in the Zurich area. Tetrachloroethylene, the most dominant chlorinated compound, was shown to originate from tertiary treated sewage and from ground spills. Giger clearly demonstrated that Grob CLSA is an excellent method to trace the source of chlorinated hydrocarbons and substituted aromatic hydrocarbons from industrial point sources. In 1979, Schwarzenbach, Molnar-Kubica, Giger, and Wakeham[25] used Grob CLSA to determine the distribution of tetrachloroethylene and 1,4-dichlorobenzene in Lake Zurich at various depths over a 12-month period. One-liter samples were stripped at 30°C for 90 minutes, and quantitation was done by

capillary GC/FID peak height measurements. Duplicate measurements over the one-year study at the 5 to 70 ng/l range had relative standard deviations of less than 10% except at the thermocline depth of the lake where concentration gradients were greatest. Using Grob CLSA data, Schwarzenbach was able to conduct an accurate mass balance for 1,4-dichlorobenzene into and out of Lake Zurich. Sewage treatment plants introduced 62 kg/year of 1,4-dichlorobenzene to the lake, whereas, the Zurich water utilities transferred 1 kg/year out of the lake. In 1977, Giger proposed[26] the use of Grob CLSA to measure volatile organics in the marine environment. In 1978, Schwarzenbach et al.[27], at Woods Hole Oceanographic Institute, along with the late Max Blumer, conducted an extensive analysis of volatile organics in coastal seawater using Grob CLSA. Since most volatile organics in seawater are present below the 10 ng/kg range, Schwarzenbach stripped 5-L samples at 35°C in order to have a higher concentration of organics for GC/MS analysis. Reproducibility for 20 selected organics in seawater samples was ± 15 to 30%.

Reinhard and McCarty at Stanford University have published many papers[28-32] using Grob CLSA as one of three analytical methods to assess advanced wastewater treatment processes and the transport of organics from groundwater injection wells. As early as 1976, Reinhard chose the following analytical methods due to the complexity of the organics in biologically treated municipal wastewater at Water Factory 21 in California. Bellar P&T analysis using a packed column GC/Hall detector system was used for haloforms and halogenated compounds with one and two carbons. Grob GC/MS CLSA was used to measure compounds of medium volatility and low water solubility. Solvent extraction with two different solvents was used to measure compounds of lower volatility and higher water solubility. Capillary separations were required except for Bellar P&T samples, and GC/MS was used to confirm all identifications. Reinhard's data clearly indicate the complexity of environmental water samples and the need for high resolution capillary separations.

In December 1979, the Exposure Evaluation Branch of HERL-CI published[3] a brief applications paper by Coleman et al. on Grob capillary GC/MS/DS CLSA of drinking water samples. Coleman reported the use of GC/MS computer procedures to automatically quantify purgeable organics in Grob CLSA data files using internal standards spiked in water samples, a computer library of 215 reference standards with narrow relative retention time windows, reverse mass spectrum library searches, and relative response factors for the 215 standards based upon single mass spectral ions. This procedure permits a laboratory to quantify three drinking water samples within a 24-hour period for 215 reference purgeable organics using twelve person-hours of time. The resulting Grob CLSA data were reported to have correctly identified 80% of the 215 reported compounds with quantitative accuracy to within ± 25% for most solvent-type organics in the 50 ng/l range. Coleman reported a GC/MS detection limit of 1 to 10 ng/l for most of the 300 to 400 organics which are identifiable by the method.

HISTORICAL BACKGROUND OF U.S. P&T METHODS

A number of P&T methods have been recently standardized by EPA. The authors will attempt to illustrate the design differences between Grob CLSA and these newer EPA P&T methods. On December 3, 1979, the U.S. EPA published in the Federal Register (FR) a set of proposed chemical methods for the analyses of pollutants[33]. The use of these proposed methods would be required for filing applications under the National Pollutant Discharge Elimination System, for State certifications, for compliance monitoring under the Clean Water Act, and for analyses of 113 organic toxic pollutants (priority pollutants) under a Settlement Agreement[34] (Natural Resources Defense Council, Inc., et al. versus Train) and under Section 304(h) of the Clean Water Act of 1977. The December 3, 1979, FR proposed the following analytical methods for the analyses of organic pollutants in water:

Method 601 Purgeable Halocarbons using packed GC/Hall

602 Purgeable Aromatics using packed GC/Photoionization

603 Acrolein/Acrylonitrile using packed GC/FID

604 Phenols

605 Benzidines

606 Phthalate Esters

607 Nitrosamines

608 Organochlorine Pesticides and PCB's

609 Nitroaromatics and Isophorone

610 Polynuclear Aromatic Hydrocarbons

611 Haloethers

612 Chlorinated Hydrocarbons

613 2,3,7,8-Tetrachlorodibenzo-p-dioxin

624 Purgeables using packed GC/MS

625 Base/Neutrals, Acids, and Pesticides using packed GC/MS

The above 15 methods are designed for the analyses of 113 specific "consent decree" organics. Method 601, 602, 603, and 624 are all Bellar P&T methods. All four P&T methods require the use of packed GC columns and different GC detectors. T.A. Bellar of Environmental Monitoring and Support Laboratory, Cincinnati (EMSL-CI) recently reported[35,36] the following two additional P&T methods:

Method 502 Purgeable Halogenated Chemical Indicators of Industrial Contamination using packed GC/Hall.

Method 503 Purgeable Aromatic Chemical Indicators of Industrial Contamination using packed GC/Photoionization.

Methods 502 and 503 are identical to Methods 601 and 602, respectively. The only difference in Methods 601 and 502, and in Methods 602 and 503 is that Methods 601 and 602 are limited to 113 "consent decree" organics. Methods 502 and 503 were developed by EMSL-CI for the EPA Office of Drinking Water (Washington, D.C.) to measure a broad spectrum of purgeable chemical indicators of industrial contamination of drinking water. EPA Method 601 will measure 29 "consent decree" organics, whereas Method 502 will measure 48 halogenated purgeable organics (chloromethane to 1,4-dichlorobenzene) at concentrations between 0.1 and 50 ug/l. Like EPA Method 601, Method 502 requires a total analysis time of 1 hour and uses a packed column GC/Hall instrument system. Method 503[36], like Method 602, is designed to measure aromatic purgeable organics with a packed column GC/Photoionization instrument system. Method 602 measures seven "consent decree" aromatics, whereas, Method 503 is capable of measuring 33 purgeable aromatic organics over a concentration range of 0.05 to 0.5 ug/l. The combined use of Bellar P&T Methods 502 and 503 will measure 81 unique purgeable organics in drinking water or raw source water with a lower limit of detection of at least 0.1 ug/l.

Methods 601 to 625 are designed for the analyses of 113 specific organics. These methods were not intended to be comprehensive methods for the in-depth analysis of a broad range of organics in water. In order to develop a comprehensive master analytical scheme (MAS), U.S. EPA (Environmental Research Laboratory, Athens, Georgia) awarded a competitive contract to Research Triangle Institute (RTI) in 1978[4-10]. This research effort was designed by EPA to insure the use of a minimum number of organic analysis procedures to analyze a very broad spectrum of organics in water. Consequently, EPA required the use of high resolution chromatography separations and broad spectrum chromatography detectors such as state-of-the-art MS/DS hardware and software. The lower detection

(LD) limits for the analysis of drinking water using MAS procedures is 0.1 ug/l.[5] For the analysis of "extractable" organics at the 1 ug/l range, the MAS recommends a BLLE procedure using methylene chloride to stir-bar extract one liter of water.[7] For the same "extractables" in cleaner water such as drinking water, the MAS recommends passing ~~four~~ three liters of water through a XAD-4 resin sorbent column and elution of adsorbed organics with ethyl ether solvent.[7] XAD-4 and XAD-2 resins differ only in pore size. Both resins have the same polymeric chemical composition and have similar sorptive characteristics. The MAS XAD-4 procedure is similar to the procedure described by Junk, et al.[37] and the XAD-EEE procedure described in this report. These three XAD procedures differ primarily in volume of drinking water used and the adjusted pH of water that is passed through the sorbent column.

For the comprehensive analysis of purgeable organics for the MAS, RTI adopted the use of the P&T capillary GC/MS/DS procedure that was previously developed by RTI and outlined in Figure 1. This procedure was intended to cover a spectrum of purgeable organics from the very volatile gases (chloromethane and vinyl chloride), such as EPA Method 601 measures, to intermediate molecular weight purgeable organics. The lower limit of detection of the current MAS P&T procedure is 0.1 ug/l for drinking water;[5] thus, according to the designers of the MAS[8], "the MAS P&T procedure does not present competition with Grob capillary GC/MS CLSA for the measurement of purgeables in drinking water at the parts per trillion level". However, since both P&T methods are intended to provide comprehensive research information on the level of purgeable organics in drinking water, the methods should be compared for differences in design and experimental performance. Such comparative information is important to chemists who must decide which P&T method (or methods) will provide the best and most cost effective analytical data. RTI has not reported research or data on the use of Grob CLSA for low to intermediate molecular weight nonpolar organics, for which

the CLSA method was designed. Instead, RTI attempted to extend Grob CLSA for the analysis of water soluble low molecular weight organics (volatile intractables), such as methanol and acetone. Not surprisingly, the method failed for this group of organics[5].

HERL-CI SCHEME FOR TRACE ORGANIC ANALYSIS

During the past two years, HERL-CI used the following three methods for the organic analysis of drinking water:

Method A - Bellar P&T GC/Hall Detector Analysis (EPA Method 601)

Method B - Grob Capillary GC/MS/DS CLSA

Method C - Liquid-Liquid Extraction (BLLE) of 10-L Samples using Methylene Chloride and Capillary GC/MS/DS Analysis

The reasons why we chose the combination of Bellar P&T (601) and Grob GC/MS CLSA to analyze purgeable organics are outlined in Figure 2. Overall, we have found that the combination of Methods 601 and CLSA provides a comprehensive, broad spectrum, cost effective, quantitative analysis of trace levels of purgeable organics in drinking water. Methods 601 (502) and CLSA are simply diagrammed in Figures 3 and 4. It is clear from these figures that the desorption modes of Bellar P&T analysis and Grob CLSA are distinctively different. Bellar P&T depends upon thermal desorption of organics from the trapping material, whereas, Grob CLSA depends upon CS_2 solvent extraction of organics from the surface of the activated carbon. It is this basic difference in method of desorption of organics from the trapping material that makes Bellar P&T Method 601 (502) and CLSA complementary in the spectrum of organics analyzed. The gaseous-type purgeable organics, which are covered up by the CS_2 solvent in the Grob CLSA, are readily quantified by the cost effective Bellar P&T method using a packed column GC/HALL instrument system. Whereas, the Grob CLSA provides a very cost

effective, quantitative analysis of purgeable organics, which elute after benzene and bromoform and which require the use of high resolution capillary columns. The data presented in this report illustrate this important principle of complementary analysis. In addition, results obtained by using Method 601, CLSA, and BLLE, above, will be compared with the XAD-2 adsorption method (XAD-EEE) of Junk et al.[37].

EXPERIMENTAL

Source of Water Samples

Drinking water samples were obtained from the Cincinnati Waterworks (CWW) on January 14, 1980, (GAC Contactor A) and on January 28, 1980, (GAC Contactor D) at sampling points into (influent) and out of (effluent) one million gallons per day (mgpd) GAC columns (Contactors) that had been on line for seven weeks and two weeks, respectively. These same GAC Contactors at CWW are described in more detail by DeMarco et al.[12]. Method 601, CLSA, and BLLE were applied to influent and effluent water samples from GAC Contactor D (as diagrammed in Figure 5). Analytical results of samples XAD-Inf., XAD-Eff., and XAD-EEE were obtained from Contactor A GAC-Inf. water on January 14, 1980. All water samples were preserved at collection with 10 mg/l of mercuric chloride and 20 mg/l of sodium sulfite. The data, however, indicate a possible problem with the use of mercuric chloride as a preservative (see RESULTS). For the XAD-2 concentration experiments, five gallons of GAC-Inf. water (see Figure 5) were brought back to HERL-CI for concentration. Bellar P&T analyses and CLSA were conducted by HERL-CI. Water samples and reagent water samples for BLLE were shipped to Battelle-Columbus Laboratories (EPA Contract 68-03-2548) for analysis. Battelle also carried out the capillary GC/MS/DS analysis of XAD-EEE extracts. Reagent water, prepared by

passing distilled water through a Millipore Super Q water purification system (all three cartridge housing units were filled with activated carbon cartridge filters), was concurrently analyzed by the same four methods. All analytical data reported in this paper have been corrected for methodology artifacts.

Bellar P&T Analysis

Purgeable, low molecular weight organohalides were analyzed using Method 601 (Figure 3), except that the purge and trap device described by Bellar and Lichtenberg[14] in 1974 was used, and the trap was packed with 60/80 mesh Tenax GC. This packing material is a deviation from the combination of Tenax GC, silica gel, and activated carbon as is specified in Method 601 and 502. Compounds such as chloromethane would not have been appreciably trapped by the sole use of Tenax GC at room temperature. Future Bellar P&T analyses from HERL-CI will be conducted using the above combination packing material.

Bellar P&T samples were chromatographed according to the following conditions:

Injector temperature	150°C
Initial column temperature	28°C
Temperature program sequence	a) Heat column from 28°C to 60°C at 40°C/min b) Hold for 1 min. c) Heat from 60°C to 160°C at 8°C/min d) Hold at 160°C
GC column	0.2 % Carbowax 1500 on Carbopak C (80/100 mesh) packed in 9 ft x 2 mm I.D. glass column

Grob Capillary GC/MS/DS CLSA

The experimental method described by Grob and Zurcher[17] was followed using the following minor modifications:

1. Water samples were collected in one-gallon screw-capped bottles.
2. Samples were analyzed in the above shipment bottles by decanting sample water down to the one-gallon mark, adding five internal standards (52 ng/l each of chlorohexane, chlorooctane, chlorododecane and chlorohexadecane, and 260 ng/l of chlorooctadecane) dissolved in 0.6 ul of acetone to the sample, and then purging the sample for two hours at 30°C.
3. The filter holder (trap) was maintained at 40°C and the heat exchanger at 80°C.

Details of HERL-CI modifications to the Grob and Zurcher CLSA method are given in another paper by Coleman et al.[11] in these proceedings and the previously published procedure by Coleman et al.[3]. The schematic in Figure 4 reflects changes in HERL-CI CLSA since the CWW samples in this publication were analyzed in January 1980. These August 1, 1980, modifications are designed to promote the CLSA of a broader and higher molecular weight spectrum of purgeable organics by maintaining a higher purge temperature and a heated all-glass system from the sample bottle to the trap. Ultrapure CS_2 from Matheson, Coleman, and Bell Chemical Company (Cincinnati, Ohio) or from Tedia Chemical Company (Fairfield, Ohio) was used without additional redistillation or clean-up.

Grob CLSA samples were separated by capillary GC according to conditions described by Coleman et al.[11]. Briefly, CLSA carbon extracts were injected (splitless) at 20°C with a capillary column flow velocity of 25 cm/sec. When the CS_2 begins to elute, the SP 2100 capillary column was heated at a rate of 2°C per minute to a maximum temperature of 250°C. Data acquisition on a Finnigan-Incos

GC/MS/DS was begun after the CS_2 finished eluting from the capillary column. The mass spectrometer was scanned at a rate of 14 to 450 amu per two seconds. Further GC/MS/DS details are described by Coleman et al.[11].

BLLE Capillary GC/MS/DS Analysis

The batch methylene chloride extraction method that is briefly outlined in the MAS[5,8] was used. If EPA Method 625 had been used, the GC/MS detection limit of 10 ug/l would have been unacceptable for the measurement of organics in these drinking water samples from CWW. The BLLE procedure below requires that 10-L water samples be collected in three sample bottles (one gallon size) and spiked with a series of deuterated internal standards at a concentration of 0.2 ug/l prior to stir-bar extraction with methylene chloride. The following experimental details are provided because it is extremely difficult to achieve acceptable sensitivity and artifact levels for the BLLE analysis of trace-level organics in drinking water:

1. Solvent Preparation. One-gallon batches of Burdick and Jackson "Distilled in Glass" methylene chloride were redistilled in a five-L flask equipped with a 60 cm x 1.8 cm ID column packed with medium size glass helices. The receiver was the original one gallon solvent bottle which was preflushed with ultra high purity N_2 (Matheson, 99.99 1/6). A positive pressure of N_2 was maintained throughout the distillation using a bubbler chamber. Methylene chloride was distilled at a rate of 1.4 to 1.8 ml/min. The first and the last 300 ml of solvent were discarded. After distillation, methylene chloride was stored under N_2 and used within three days for BLLE.

2. Sample Extraction. Ten liters of drinking water were extracted in the original one gallon sample bottles by first removing all but 3.3 L of sample water from each of three sample bottles, then adding 33 ul of

a mixture of deuterated internal standards (0.2 ug/l)[38], adding a 3-in. teflon stirring bar, stirring the water sample at maximum stable speed, and adding concentrated sulfuric acid until the acidity was lowered to pH 2 to 2.5. Three 40-min solvent extractions were made using 250 ml, 100 ml, and 100 ml of redistilled methylene chloride. Solvent was removed after each extraction using an all glass andteflon pipet-type device and about 5 in. of Hg vacuum.

3. Solvent Evaporation. The stir-extraction, above, of 10 L of drinking water in three sample bottles yields approximately 1200 ml of methylene chloride. Two Kuderna-Danish (KD) apparatuses were used to concentrate the solvent to a volume of about 4.5 ml which was fractionated into an acids fraction (derivitized with diazomethane) and a neutrals fraction according to the procedure described by Lucas et al.[38]. BLLE samples were chromatographed on a 40-M x 0.25 mm I.D. SP1000 WCOT capillary column (prepared by Battelle) according to the following conditions:

Injector temperature	250°C
Initial oven temperature (hold)	50°C (6 min)
Temperature program rate	2°C/min
Upper temperature limit	225°C
Injection volume	2 ul sample + 1 ul heptane
Transfer line temperature	250°C

XAD-EEE Capillary GC/MS/DS Analysis

The grab sample method described by Junk et al.[37] was used for the concentration of organics with the following modifications:

1. XAD-2 resin sufficient for both CWW GAC Contactor A and D experiments

(see Figure 5) was cleaned up by consecutive 24-hr Soxhlet extractions with methanol, acetonitrile, ethyl ether, and methanol. Clean resin was stored wet under methanol until prior to packing columns.

2. Two columns were set up; one column for 10 L of CWW XAD-Inf. water, and the second for 10 L of Super Q reagent water. Each column was 2.7 cm in diameter by 6.5 cm in height. A silanized glass wool plug was placed on the bottom of the empty column.

3. The resin was removed from the methanol storage bath and slurried into a beaker of Super Q reagent water. The resin was then rinsed four times with Super Q reagent water. Next the resin (37 cm^3) in the beaker was slurried into the glass column, which was filled with reagent water. Silanized glass wool was placed on top of the resin which was always kept wet with reagent water. The column resin was then rinsed with one L of Super Q reagent water.

4. Ten liters each of CWW sample and reagent water were adjusted to pH 2 with 20 ml of 12 N sulfuric acid.

5. Each acidified sample water and reagent water were passed through each respective XAD-2 column at a flow rate of approximately 28 ml per min. Each column was immediately rinsed with 200 ml of pH 2 reagent water. Sample water and reagent water that passed through each respective XAD column were labeled XAD-Eff. and were later analyzed by HERL-CI using EPA Method 601 and Grob CLSA, and by Battelle-Columbus Laboratories using BLLE.

6. Three bed volumes of freshly redistilled ethyl ether were used to elute the adsorbed organics from the XAD-2 resin. This ethyl ether eluant was labeled XAD-EEE.

7. The sodium sulfate drying procedure of Junk et al.[37] was used.

8. The ethyl ether eluant was evaporated to 1 ml (KD) and shipped to Battelle-Columbus for capillary GC/MS/DS analysis under EPA contract 68-03-2548.

All capillary GC/MS/DS parameters for the analysis of XAD-EEE samples were the same as previously described for BLLE samples.

RESULTS

Chromatograms using Method 601, Grob CLSA, and BLLE are presented for GAC-Inf. and GAC-Eff. water only, due to manuscript space limitations. Unfortunately, the XAD-2 ethyl ether eluant (XAD-EEE) samples from CWW GAC Contactor D were heavily contaminated with chemical artifacts from the XAD-2 resin. Since we had good samples and data files using all four methods taken at the same points at GAC Contactor A at the CWW on January 14, 1980 (two weeks prior to CWW Contactor D samples), we have presented, instead, analytical results on the XAD-Inf., XAD-Eff., and XAD-EEE samples from Contactor A water. Basically, this change from Contactor D GAC-Inf. water to Contactor A GAC-Inf. water is simply a difference in sampling CWW raw Ohio River water on dates differing by two weeks. Comparison of CWW GAC-Inf. water samples on January 14, 1980, and January 28, 1980, using Grob CLSA and BLLE analyses shows that water samples on these two dates are quite similar, except that there was a slightly higher level of alkyl-substituted benzenes in the January 28, 1980, water samples.

Total organic carbon (TOC) measurements of combined volatile and non-volatile organics were determined on GAC-Inf. and GAC-Eff. water from CWW. On January 14, 1980, the TOC of GAC-Inf. to Contactor A was 1.9 mg/l and of GAC-Eff. water was 1.2 mg/l. This represents a removal of 37% total organic carbon by the GAC (7 weeks old) in Contactor A. The TOC of Contactor D water on January 28,

1980, (GAC was in use for two weeks) showed a corresponding reduction from 1.6 mg/l to 0.2 mg/l, or a removal of 87% TOC.

Results of Bellar P&T analysis (Method 601) are presented in Table 1, and representative chromatograms in Figure 6. Only six halogenated organics were detected due to the low level of purgeable organics in GAC-Inf. water. All six compounds were "consent decree" organics with an average concentration of 16 ug/l. No organics were detected in the corresponding GAC-Eff. water. This would represent a 100% removal by GAC Contactor D at CWW. According to EPA Method 601, an additional 23 (29-6) organics would have been detected in GAC-Inf. water if present in concentrations above 0.06 ug/l. EMSL-CI Method 502 would have detected an additional 42 (48-6) halogenated organics if they had been present above 0.1 ug/l. Table 1 also shows the effect of the 37-cm^3 XAD-2 analytical column in removing halogenated purgeable organics from XAD-Inf. water. Overall, Table 1 indicates that the 1 mgpd GAC Contactor D at CWW was more effective in removing organics than was the small XAD-2 analytical column.

Results of Grob capillary GC/MS/DS CLSA are presented in Table 2. Grob CLSA detected 107 purgeable organics in GAC-Inf. water (Contactor D). Quantitative results of organics listed in Table 2 that have the designation "S" under "Quan. Method" are based upon actual relative response factors of reference compounds, as compared to the internal standard, chlorododecane, which was initially spiked in each water sample at 52 ng/l. A total ion current area relative response factor of one (chlorododecane, IS) is assumed for the compounds which do not have the "S" designation in Table 1. As mentioned earlier, the average concentration of the non-trihalomethane organics in GAC-Inf. water according to CLSA was 9.2 ng/l. The average concentration of these same organics in GAC-Eff. water was 1.8 ng/l. If the MAS P&T procedure had been used on GAC-Inf. water (Contactor D), probably only five compounds (four trihalomethanes and 1,1,1-trichloroethane)

would have been detected. This prediction is based upon the MAS GC/MS lower detection limit of 0.1 ug/l.[5] The 80% removal of the CLSA organics in GAC-Eff. water by CWW GAC Contactor D shows surprisingly good agreement to the 87% removal based on TOC cited above. Since most of the TOC material is probably of humic origin (and therefore not accessible to Grob CLSA), these data seem to indicate that GAC Contactor D is removing the same percentages of purgeable organics and humic material. The XAD-Inf. and XAD-Eff. data in Table 2 indicate that the 37-cm^3 XAD-2 analytical column removed 79% of these same Grob CLSA organics. Accordingly, CWW GAC Contactor D and the XAD-2 analytical column are doing similar jobs (80%, 79%) in removing the organics which can be measured by Grob CLSA in GAC-Inf. and XAD-Inf. water. The ability of Grob CLSA to directly measure the effect of XAD resin as a unit process is clearly illustrated in Table 2. Grob CLSA is also an excellent method to determine if XAD-2 resin is adequately cleaned-up (See Figure 5) for analytical use as an adsorbent by measuring purgeable organics in reagent water before and after passage through an XAD column.

The chromatograms in Figure 7 are arranged to illustrate the Grob CLSA differences between GAC-Inf. and GAC-Eff. water. Note that the levels of internal standards (IS) in Figure 7 are the same. Also, that two of the first detectable organics that elute after the CS_2 solvent are isopropyl ether and chloroform. If more volatile nonpolar organics had been present, such as chloromethane, vinyl chloride, and methylene chloride, they would have been covered up by the CS_2 solvent peak. These more volatile organics would have been detected, however, by the Bellar P&T analysis (Method 601) of these same CWW samples (see Table 1 and Figure 6) if we had used a trap packed with Tenax, silica gel, and activated carbon.

Results of BLLE capillary GC/MS/DS analysis of GAC-Inf. and GAC-Eff. water

are presented in Tables 3 and 4, which correlate with the chromatograms shown in Figures 8 and 9. Fifty-one and 38 organic compounds were identified in the neutral and methylated acid fractions of GAC-Inf. water. These BLLE samples are notably low in solvent artifacts due to the elaborate methylene chloride purification steps employed. Meticulously clean solvents, reagents, and glassware are necessary for reproducible GC/MS analysis of BLLE samples of trace organics in drinking water. Figures 8 and 9 clearly illustrate the high level of artifact free performance which has been achieved. The peaks labeled "IS" are deuterated internal standards (0.2 ug/l level) which were added to the water before extraction. The peak marked "IS HEB" is hexaethylbenzene, an internal standard, which was also added at the 0.2 ug/l level prior to GC/MS analysis. Artifacts which are due to aqueous extraction or extract fractionation are indicated by special symbols in the figures. Divinylmercury (C_4H_6Hg) was present in GAC-Inf. water according to BLLE (methylated acid fraction). Divinylmercury also appeared in some of the BLLE blanks of reagent water. The presence of divinylmercury may be due to a chemical reaction between the preservative, mercuric chloride, and certain organics in the water samples.

The contamination of the XAD-EEE extract from the Contactor D experiment by XAD-2 resin was so severe that the resulting GC/MS data files were of no value. These artifacts are quite typical of what we have seen on a number of occasions when analyzing XAD-2 generated organic concentrates. Since XAD-2 resin and XAD-4 resin are widely used for the concentration of organics from water (the MAS "extractables" method uses a similar resin, XAD-4, to concentrate organics from 4 liters of drinking water), and since we are not aware of literature documentation of the specific contaminants one generally encounters, the abbreviated listing in Table 5 may be of some use to the reader. Capillary GC/MS/DS analysis of the XAD-EEE extract from the Contactor A experiment is

presented in Tables 6 and 7. A total of 58 organic compounds were identified in the neutral and methylated acid fractions of this XAD-EEE extract.

DISCUSSION

The data presented above on these and other water samples will help HERL-CI determine the authenticity of organic concentrates derived from reverse osmosis, lyophilization, and XAD adsorption such as those which were produced from the same GAC-Inf. water on January 14, 1980, and January 28, 1980. For our health effects research, it is clear to us that we will not be successful in producing representative organic concentrates of water for biological screening tests, if we do know how to conduct state-of-the-art organic analysis of the "starting material" - drinking water.

The contamination problem that we encountered with XAD-EEE sample from Contactor D water on January 28, 1980, and not from Contactor A water two weeks earlier has been a consistent problem in our use of XAD-2 resin over the past six years. The Grob CLSA data of XAD-Eff. water from Contactor A and D experiments indicate that the XAD-Eff. water was not contaminated by XAD-2 resin (see Table 2). Therefore, we have obviously contaminated the XAD-EEE sample from Contactor D during the ethyl ether elution step, even though the same procedure was used for both January 14 and January 28 experiments. Hopefully the XAD-4 resin adsorption method described in the MAS for the measurement of "extractable" organics in drinking water will be designed to absolutely prevent such contamination from XAD resin during the ethyl ether elution of adsorbed organics.

Two hundred fifteen organic compounds have been purchased as authentic standards and analyzed by Grob CLSA. For those compounds listed in Table 8, experimental response factors and chromatographic behavior have been determined so that all CLSA data files can be automatically searched for these 215 compounds using reverse library search software. For the purposes of this manuscript on

the comparison of Grob CLSA with Bellar P&T, BLLE, and XAD-EEE, an attempt has been made to summarize the comparative differences of the four selected methods in Tables 9 and 10 using one water sample; GAC-Inf. water from Contactor D (Contactor A for XAD-EEE). Reverse library computer searching for the 215 organics was performed automatically on the CLSA GC/MS data file of GAC-Inf. water, and 64 organics were detected and quantified by the Incos data system. The method described by Coleman et al.[11] was used. One hundred seventy-one of the 215 organics were not found. This negative information is very valuable in that several of the 171 organics not detected in GAC-Inf. water are toxic. For example, Coleman reports[11] in this volume that 2,2',4,4',6,6'-hexachlorobiphenyl (a PCB isomer of molecular weight 358), one of the 171 organics not detected, can be measured in drinking water by Grob GC/MS CLSA at a concentration of 2 ng/l. The standard deviation for the measurement of this PCB isomer at 6.2 ng/l concentration (16 replicates, 59% recovery efficiency) was + 1.1 ng/l. For drinking water treatment researchers and toxicologists, this type of reproducibility and sensitivity is important. However, the drinking water consumers in Cincinnati are perhaps the most gratified group over the low GC/MS detection limits of Grob CLSA, since they probably dislike drinking PCB isomers. If this PCB isomer were detected in GAC-Inf. water at 2 ng/l, then the combined concentration of all Arochlor PCB isomers in the drinking water would have been dramatically higher than 2 ng/l. Unfortunately, we have detected PCB isomers on previous occasions in several drinking water samples from other major cities using Grob GC/MS CLSA. The analogous limits of detection pertaining to BLLE and XAD-EEE is not available, since it is very difficult and time consuming to obtain quantitative data using BLLE and XAD adsorption.

TOC measurements indicate that CWW GAC Contactor D was 87% effective in removal of organics, whereas, CLSA indicates that Contactor D was 80% effective in removal of purgeable organics. CLSA also indicates that the XAD-2 analytical column was 79% effective in removal of purgeable organics.

Table 9 provides us with information on overlap between the four methods. For example, dibromochloromethane and bromoform were detected by all four methods. However, only Bellar P&T and Grob CLSA provided quantitative results.[11,33] Of the 12 carboxylic acids (including 2,4-dichlorophenoxyacetic acid) that were identified by BLLE and XAD-EEE analyses, none were observed in Grob CLSA data. BLLE and XAD-EEE analyses detected the presence of 3-nitrotoluene and 2,4-dinitrotoluene in GAC-Inf. water, but Grob CLSA did not detect these important compounds. Surprisingly, BLLE missed four isomers of ethyldimethylbenzene that Grob CLSA and XAD-EEE analyses detected. Perhaps these alkylated benzene isomers were lost during the evaporation of 1200 ml of BLLE methylene chloride down to 0.5-ml volume. BLLE and XAD-EEE analyses produced similar GC peak heights for most methylated acids and nitrotoluenes.

Table 10 provides a greater depth of comparative physical-chemical information than any other table or figure. Overall, 183 different organics were detected in GAC-Inf. water by all four methods. Six organics were detected by Bellar P&T, 107 by Grob CLSA, 90 by BLLE, and 58 by XAD-EEE. As compared to 183 total organics, 3% were detected by Bellar P&T, 58% by CLSA, 49% by BLLE, and 32% by XAD-EEE. Of consent decree[33,34] organics, Bellar P&T detected 5%, Grob CLSA detected 20%, BLLE detected 10%, and XAD-EEE detected 5%. The EPA Office of Drinking Water published[37] a list of "chemical indicators of industrial pollution" (1978) as a yardstick-measure to determine if a drinking water supply would be required to use GAC to remove toxic pollutants from potable water. Of the 62 organics or organic classes on this list, Bellar P&T detected 3%, Grob CLSA

detected 27%, BLLE detected 16%, and XAD-EEE detected 8%. In summary, for these samples of drinking water, Grob CLSA has resulted in the quantification of a larger number and higher percentage of the organics that EPA is currently monitoring than the three other methods. This summary statement would not be accurate if the concentration of "consent decree" organics and "chemical indicators of industrial pollution" had been greater than 40 ng/l. At concentrations greater than 40 ng/l, Method 601 would have detected 28 (26% of 113) "consent decree" organics and EMSL-CI Method 502 would have detected 43 (69% of 62) "chemical indicators of industrial pollution". At concentrations greater than 0.1 ug/l, the MAS P&T and XAD adsorption procedures should have detected a majority of the "consent decree" organics and "chemical indicators of industrial pollution".

The above statistics do not provide an overview of the physical-chemical differences of the four methods. Table 10 indicates that Grob CLSA quantified more aliphatic hydrocarbons and aromatic hydrocarbons than the other three methods combined. However, CLSA detected a lower number of nitrogen compounds and oxygenated compounds than either BLLE or XAD-EEE. Concerning specific functional groups, Grob CLSA detected a greater number of alkanes, alicyclic hydrocarbons, alkylated benzenes, indeno hydrocarbons, naptheno hydrocarbons, aldehydes, quinones, aliphatic esters, ethers, oxygen-containing heterocycles, halogenated aliphatics, halogenated aromatics, and halogenated ketones. However, BLLE detected a greater number of water soluble compounds such as alcohols, glycols, ketones, halogenated ethers, aromatic carboxylic acids, amides, nitriles, halogenated phenols, and phosphates. Table 10 also indicates that aliphatic carboxylic acids (fatty acids) were equally well detected by BLLE and XAD-EEE. Overall, XAD-EEE analysis did not perform as well as BLLE analysis. In summary, Table 10 indicates that more toxic or potentially toxic species may be

quantified by Grob CLSA than by the other three methods, but that Bellar P&T, Grob CLSA, and BLLE have optimal performance for different classes of organics. Thus, it is clear that Bellar P&T (Method 601), Grob CLSA, and BLLE are important complementary methods. For this reason, HERL-CI will continue to require the use of all three methods for health effects research water samples.

The physical-chemical data in Table 10 also provide valuable information about the optimum choice of liquid phases for the GC separation of organics in CLSA, BLLE, and XAD-EEE extracts. Satisfactory separation results can be obtained for the non-polar organics in CLSA extracts using both non-polar (methyl silicone) and polar GC liquid phases. The predominance of oxygenated polar organics in BLLE and XAD-EEE extracts require the use of polar liquid GC phases for optimum separation results. Chemists should not forget that the splitless injection of solvent extracts on WCOT capillary columns requires the GC liquid phase be a liquid (not a solid) at the temperature needed to achieve the correct solvent effect performance. For example, the use of CS_2 as a CLSA extraction solvent requires a GC oven temperature of 20°C or less for a satisfactory solvent effect. Thus, the capillary column liquid phase must also be a liquid at 20°C. Consequently, the use of SP1000 or Carbowax 20M liquid phases for the capillary splitless injection of CS_2 extracts would be unsatisfactory because these polar phases are a semi-solid at 20°C. Unfortunately, the operating temperature range (minimum and maximum temperatuares) of most commercially available polar capillary columns is unacceptable for the splitless injection of CLSA, BLLE, and XAD-EEE extracts. This limitation of too high of a minimum temperature may be overcome by using a solvent exchange step (with a higher boiling solvent) or by adding a higher boiling solvent to a CLSA, BLLE, or XAD-EEE extract prior to splitless injection. Both of these approaches lead to complete masking and/or partial loss of many early eluting components.

"Cost versus benefit (number of organics measured)" is an important consideration when comparing methods. However, we have not been able to devise a fair way to make this type of comparison for BLLE and XAD-EEE analyses. The data in this report is not quantitative and the limits of detection are unknown for these two methods, therefore, it is difficult to determine a fair basis for comparison with Bellar P&T and Grob CLSA. Precision and accuracy data has been previously reported for Method 601[33] and Grob CLSA[11]. However, some cost information on Bellar P&T and Grob CLSA can be provided. For these calculations, the apropriate cost for the analysis of GAC-Inf. water by Bellar P&T (Method 601 or 502) is $85 and by Grob CLSA is $460. Even though only six organics were detected using Bellar P&T analysis, 48 halogenated organics above 0.1 ug/l according to EMSL-CI Method 502 could have been detected. One hundred and seven organics were detected by Grob CLSA plus 171 organics (215-64) were not present above our CLSA limits of detection. Therefore, Grob CLSA could have detected 278 organics in GAC-Inf. water. Following this logic, the average cost to quantify an organic by EMSL-CI Method 502 and by Grob CLSA is approximately $2. Even though these figures would indicate that Bellar P&T Method 502 and Grob CLSA have a similar "cost versus benefit" ratio, the methods are not similar in the complexity of instruments required to perform an analysis. However, in considering the complementary nature and "cost versus benefit" figures of Bellar P&T analysis (Method 601 or 502) and Grob CLSA, both methods are used for important health effects research water samples, especially for studying a water treatment unit process such as GAC adsorption or ozone disinfection.

To further illustrate the effectiveness of CLSA to monitor the fate of purgeable organics in water, the Grob CLSA chromatograms (Figure 10) of a CWW sample before and after ozone treatment (Ozone-Inf. and Ozone Eff. water, respectively) are presented. The predominant oxidation of specific, trace-

level, alkyl-substituted and halogen-substituted benzenes in this drinking water sample would not have been apparent using the other three methods or MAS procedures. Ozonolysis water treatment experiments conducted by the EPA Drinking Water Research Divison (Cincinnati, OH) and analytical Grob CLSA conducted by HERL-CI indicate that the reduction of purgeable organics in Figure 10 is due to chemical oxidation and not gas-phase stripping (ozone-oxygen). The apparent chemical oxidation of these organics indicates a possible reduction in toxic organics in ozonated drinking water. However, this is not to imply that the reduced amounts of purgeable halogenated and aromatic compounds detected in this ozonated water by Grob CLSA will provide evidence of a reduction in long-term health effects. Such a determination would also require the comprehensive measurement of ozone reaction products and the toxicological effects of ozonated drinking water. Grob capillary GC/MS/DS CLSA, however, does provide highly reproducible, quantitative information of many unit process effects (GAC, ozonation, etc.) for one small group of compounds in drinking water - purgeable organics.

CONCLUSIONS

Future Comprehensive Analytical Scheme For Purgeable Organics

The analysis of purgeable organics will continue to be important in future years, because many industrial pollutants are readily measured by P&T procedures. State-of-the-art knowledge of comprehensive purgeable analytical methods has reached a sufficiently high level that now allows environmental chemists to design superior analytical schemes for the comprehensive analyses of purgeables in drinking water. This comprehensive scheme, in our estimation, should consider the following requirements which are evident in the data presented:

1. Bellar P&T methods, such as EPA Methods 601[33] and 502[35], provide adequate sensitivity, GC resolution, detector specificity, and overall method reproducibility to cost-effectively quantify low molecular weight halogenated purgeable organics in drinking water. Furthermore, gaseous-type halogenated organics such as chloromethane and vinyl chloride are readily measured by the "combination" trap (Tenax - silica gel - activated carbon)[33,35], which is required in Methods 601 and 502. The above advantages and data indicate that EPA Methods 601 and 502 will continue in the future to be widely used by U.S. drinking water laboratories. In addition, our data indicate that if Grob closed-loop stripping analysis (CLSA) is used to measure purgeable organics in water, the Bellar P&T Method 601 (or 502) should also be used to measure low molecular weight halogenated organics (chloromethane, vinyl chloride, chloroform, etc.) which are not amenable to Grob CLSA.
2. High resolution capillary columns are required to separate the hundreds of alkyl-substituted and halogen-substituted aromatic compounds which are often present in drinking water (see Table 2 and Figure 10). Future data may show that, due to the complexity of environmental water samples containing substituted aromatic isomers, it is extremely difficult to measure purgeable substituted aromatics using packed GC columns and a photoionization detector such as are required in EPA Methods 602[33] and 503[36]. Instead, capillary GC/MS/DS analysis such as Grob CLSA or the MAS RTI P&T procedure will be necessary for these substituted aromatic compounds.
3. If future researchers find that statement 1, above, is correct, then the required capillary GC/MS/DS procedures described in statement 2

should be developed to quantitatively measure a broad spectrum of purgeable organics from benzene, toluene, and isomers of dichlorobenzene to as high a molecular weight range as is practical. Higher purging temperatures and optimized trapping materials should be developed and used. There seems to be a misconception today in the thinking of some environmental chemists that batch liquid-liquid extraction (BLLE) procedures or XAD adsorption procedures (XAD-EEE) will cost-effectively measure low levels (1 to 100 ng/1) of purgeable organics such as alkyl- and halogen-substituted indans, tetrahydronaphthalenes, and biphenyls. These organics are difficult to quantitatively measure in drinking water by BLLE and XAD-EEE due to interferences from concentrated solvent impurities, losses of these organics during Kuderna-Danish evaporation, and to the overall insensitivity of BLLE and XAD-EEE. Therefore, the use of BLLE or XAD-EEE for these purgeable organics is very difficult and costly. A comprehensive capillary GC/MS P&T procedure, such as Grob CLSA or the MAS P&T procedure, should be optimized to quantitatively measure trace amounts of these higher-molecular weight aromatic compounds in drinking water.

4. The MAS RTI P&T method attempts to use one P&T procedure to achieve the comprehensive, combined results of both Method 601 (or 502) and Grob capillary GC/MS/DS CLSA. From a design viewpoint, the MAS procedure may poorly measure highly volatile compounds (such as chloromethane and vinyl chloride) which Methods 601 and 502 readily measure. This is due to the use of a removable-type Tenax (only) cartridge at room temperature. Furthermore, it is not certain that the MAS P&T procedure will measure the organics listed in statement 3 which are readily

measurable by Grob CLSA. There is a need to systematically compare EPA Method 601 (502) and Grob capillary GC/MS/DS CLSA to the MAS RTI P&T procedure and to optimize a capillary GC/MS P&T procedure that meets the basic requirements of statement 3. Such a comparison should also include BLLE, EPA Methods 602 and 503 and the MAS XAD-4 procedure. The cost effectiveness of each method should be computed.

Future Use of Grob CLSA

Even though Grob capillary GC/MS/DS CLSA is one of the first operational and viable comprehensive purgeable analytical methods for drinking water, the subsequent large number of purgeable organics measured by CLSA comprise only a very small weight of the total mass of organic material present in potable water. The data, however, indicates that the use of Grob capillary GC/MS/DS CLSA and Bellar P&T analysis (Method 601 or 502) provide a viable and useful approach for studying trace-level amounts of a surprisingly wide range of purgeable organics in drinking water. Some of the advantages, disadvantages, and general features of the CLSA method are listed here:

Advantages:

1. The method is simple, straightforward, and rapid. A water sample can go from cold storage to GC/MS injection of the CLSA filter extract in about 2 1/2 hours. Sophisticated, electronic "black boxes" are not required for CLSA. No alteration of a standard capillary GC/MS/DS (equipped with a Grob-type splitless injector) is required. Overall, CLSA equipment costs about $1300.
2. The method is ultra-sensitive. Good mass spectra can be obtained on most purgeable compounds in the 1 to 10 ng/l range. The GC/MS detection limit of some PCB isomers is 2 ng/l.

3. Blanks are extremely clean. The sample is extracted from the activated carbon filter with only 12 ul of carbon disulfide.

4. Glass or fused-silica capillary columns coated with methyl silicone liquid phases can be used with CLSA carbon filter extracts for a year or more without developing sample-induced degradation of column performance. This is in direct contrast to the injection of BLLE and XAD-EEE extracts on similar capillary columns.

5. The method is relatively trouble free. The most frequent problem (about once every 3 months at HERL-CI) has been contamination of the closed-loop with high molecular weight organics from heavily contaminated water samples. Muffling the glass and metal components of the loop at 450°C for 2 hours corrects this problem.

6. On a per-compound-quantified basis, the method is highly cost effective. Once initiated, sample purging, GC/MS data acquisition, and automatic computerized quantification methods proceed virtually unattended. Solvent extraction of the activated carbon trap requires approximately 10 minutes. Overall, three drinking water samples can be automatically quantified for 215 organics in 24 hour period using 12 person-hours of labor.

Disadvantages:

1. The range of compounds effectively measured by Grob CLSA is somewhat limited:

   a) Highly volatile compounds such as chloromethane, vinyl chloride, methylene chloride, and chloroform are poorly recovered and/or covered up by the CS_2 extraction solvent. Therefore, Bellar P&T Method 601 (or 502) should also be used with CLSA to provide a comprehensive analysis of purgeable organics.

b) Moderate and highly polar or ionizable organic species are either poorly purged or not recovered at all.

2. Highly contaminated samples, such as industrial effluents, may overload the 1.5 mg activated carbon trap and contaminate the closed-loop. A larger capacity 5.0 mg trap, however, is now available from Bender and Holbein Company in Zurich.

3. The method requires the development of new laboratory skills (extraction of the trap) before the method can be effectively implemented. This may account for the surprisingly slow acceptance of Grob CLSA in the U.S. as compared to European countries. While the CLSA procedure can become highly routine in the hands of competent technicians, the method is demanding of careful and consistent manipulations.

4. There is currently no U.S. commercial supplier of the Grob-designed activated carbon filters or filter holders. In addition, there is no worldwide supplier of an integrated, self-contained CLSA apparatus. CLSA components must be purchased from a number of suppliers.

5. Grob CLSA has not been comprehensively researched to optimize analytical conditions and apparatus since Grob and Zurcher[12] standardized the procedure in 1976. It is suggested that Grob CLSA be optimized to measure purgeable compounds from benzene, toluene, and dichlorobenzenes to as high a molecular weight range as is practical.

Additional Features:

1. Grob CLSA is especially suitable for automatic quantification procedures using state-of-the-art GC/MS/DS. The method provides highly reproducible relative retention time data (± 0.2%) and clean mass spectra, which are important for highly successful automatic GC/MS/DS software procedures.

2. The five internal standards added before sample purging greatly facilitate the requirement for good quality control and the monitoring of recovery efficiencies.

This report shows that many compounds which are not amenable to Bellar P&T and Grob CLSA (due to low stripping efficiencies caused by polarity, ionizability, and/or non-volatility) can be effectively analyzed using a large sample volume (10 L), BLLE, and ultra-clean laboratory techniques. The described BLLE procedure has produced extremely clean blanks and an apparent GC/MS detection limit of 5 to 50 ng/l for a wide variety of extractable organic compounds.

The described XAD-2 ethyl ether elution (XAD-EEE) procedure (10 L water sample) did not perform nearly as well as the above BLLE procedure. This XAD adsorption procedure has also been shown to erratically contaminate extracts during the ethyl ether elution phase of the procedure. Consequently, the use of XAD adsorption procedures is not recommended (especially for the measurement of alkyl-substituted aromatic compounds in drinking water) unless this type of contamination can be absolutely prevented. The use of XAD-2 or XAD-4 resin to measure alkyl-substituted benzenes, indanes, tetrahydronapthalenes, and napthalenes is especially difficult due to the documented contamination artifacts from XAD-2 and XAD-4 resin in this report (see Table 5). A P&T method such as Grob CLSA is superior for this group of substituted aromatics.

This report presents experimental data which may be useful to the many research laboratories that are developing and using comprehensive analytical methods for the measurement of organics in drinking water. The development of comprehensive analytical methods is expensive. It is especially important in this coming era of diminishing monetary support for drinking water research that comprehensive methods of organic analysis be 1) broad spectrum, 2) sensitive, 3) cost-effective, and 4) scientifically sound. Hopefully, this report will

stimulate renewed thinking along these lines.

The data presented suggests that the combined use of Bellar P&T Method 601 (502) and Grob capillary GC/MS CLSA (two cost-effective P&T methods) measures a number of organics (at concentrations between 10 and 100 ng/l) that the MAS P&T method and MAS XAD-4 adsorption method cannot measure.[8] The data also suggests that the combined use of Bellar P&T Method 601 (502) and the described Grob CLSA and BLLE procedure will measure a considerably greater number of organics (both toxic and non-toxic) in drinking water than the combined use of the MAS P&T and MAS XAD-EEE procedures[4-10].

Experimental data on samples of drinking water from CWW indicates that twice as many "consent decree" organics[33] and "chemical indicators of industrial pollution"[39] were detected and quantified by Grob CLSA than by Bellar P&T, BLLE, and XAD-EEE analysis. Furthermore, Grob CLSA produced this superior analysis at a low cost-per-compound-analyzed figure. The comparative data presented verify the words used by Professor K. Grob, M. Reinhard, L. Stieglitz, and G. Piet to describe Grob CLSA - "The method works". This is the primary reason why Grob CLSA continues to increase in worldwide popularity.

This report has attempted to present a brief review of U.S. P&T methods and to point out design differences of each method. Interested North American environmental chemists may find the detailed historical review of Grob CLSA particularly useful. Finally, experimental data from our health effects research has been presented to illustrate some basic differences between Grob CLSA, Bellar P&T (Method 601), BLLE, and XAD-EEE analyses. Even though the experimental data from these CWW samples does not validate or invalidate any of the four tested methods, the data demonstrates some important differences in the analytical performance which one might expect of each of these methods. Overall,

the data indicate that the combined use of Bellar P&T (EPA Methods 601 or 502), Grob capillary GC/MS/DS CLSA, and capillary GC/MS/DS BLLE analyses provide useful information on drinking water treatment unit processes such as the purification of water with one mgpd GAC Contactors.

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b) GAC-Eff. Water was collected after passage through the 1 mgpd GAC contactor at CWW;

c) XAD-Inf. Water was GAC Inf. water which was brought back to HERL-CI for subsequent adsorption on a 37 cm^3 XAD-2 analytical column;

d) XAD-Eff. Water was collected after passage of XAD Inf. water through the 37 cm^3 XAD-2 column.

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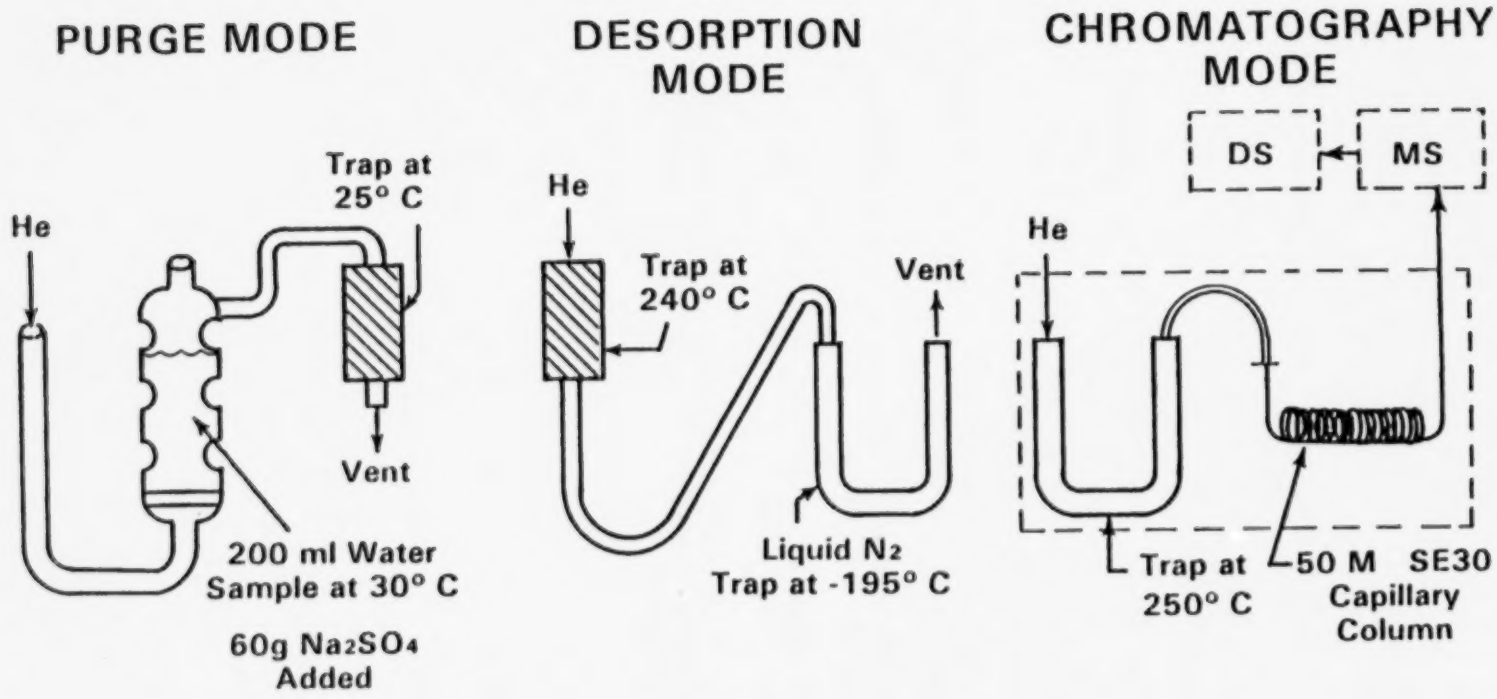


Figure 1

Fundamental Schematic of EPA Master Analytical Scheme P&T Method (RTI Method)

Method A - Analysis of 5 ml Water Samples using EPA Method 601 (Bellar Purge and Trap Analysis) for Quantification of 23 Halogenated Low Molecular Weight (Chloromethane through Bromoform) Organics.

5 ml Sample

ADVANTAGES:

1. Low Cost - Packed GC Columns/Electro-Conductivity Detector
2. Fast - 20 minutes for Bromoform to Elute.
3. Well Researched and Accepted Method.
4. Good Quality Control Procedures.

DISADVANTAGES:

1. Very Few, Considering Cost/Organic

Method B - Analysis of 1-L Water Samples using Grob CLSA for MS Quantification of over 215 Organics and Qualitative Identification of over 400 Organics.

1 Liter Sample

ADVANTAGES:

1. Good MS Sensitivity - Detection Limit of 1 to 10 ng/l.
2. Good Reproducibility - Internal Standards are spiked in Water Prior to Purging; Accuracy of ± 25% for most Solvent Type Organics at the 50 ng/l Level.
3. Excellent Method for Control of Unit Processes such as;
   A) Use of Granular Activated Carbon.
   B) Disinfection with Ozone, Chlorine, Chlorine Dioxide, and Chloramines.
   C) Source Contamination of Drinking Water Supplies due to Industrial Spills and/or Discharges.

DISADVANTAGES:

1. Expensive
   A) Cost per capillary GC/MS/DS CLSA - $460, or
   $460 ÷ 215 Organics = $2 per Organic.
   B) Cost per capillary/FID CLSA - $80
2. Sample Matrix Interferences.
3. Activated Carbon Trap may become Overloaded with Organics in Industrial Effluents

Figure 2 HERL-CI Approach to Analysis of Purgeable Organics in Drinking Water

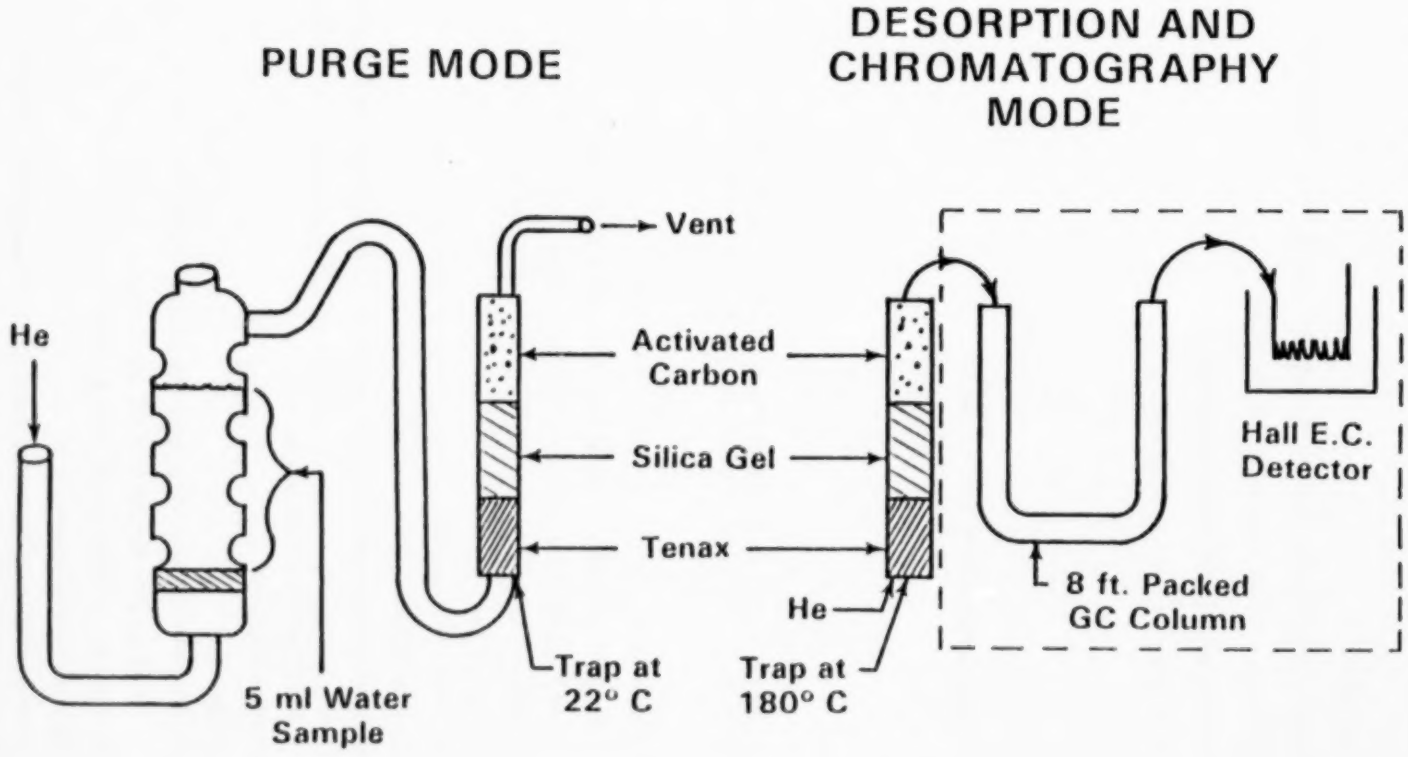


Figure 3

Fundamental Schematic of EPA Method 601 and 502 (Bellar P&T Method)

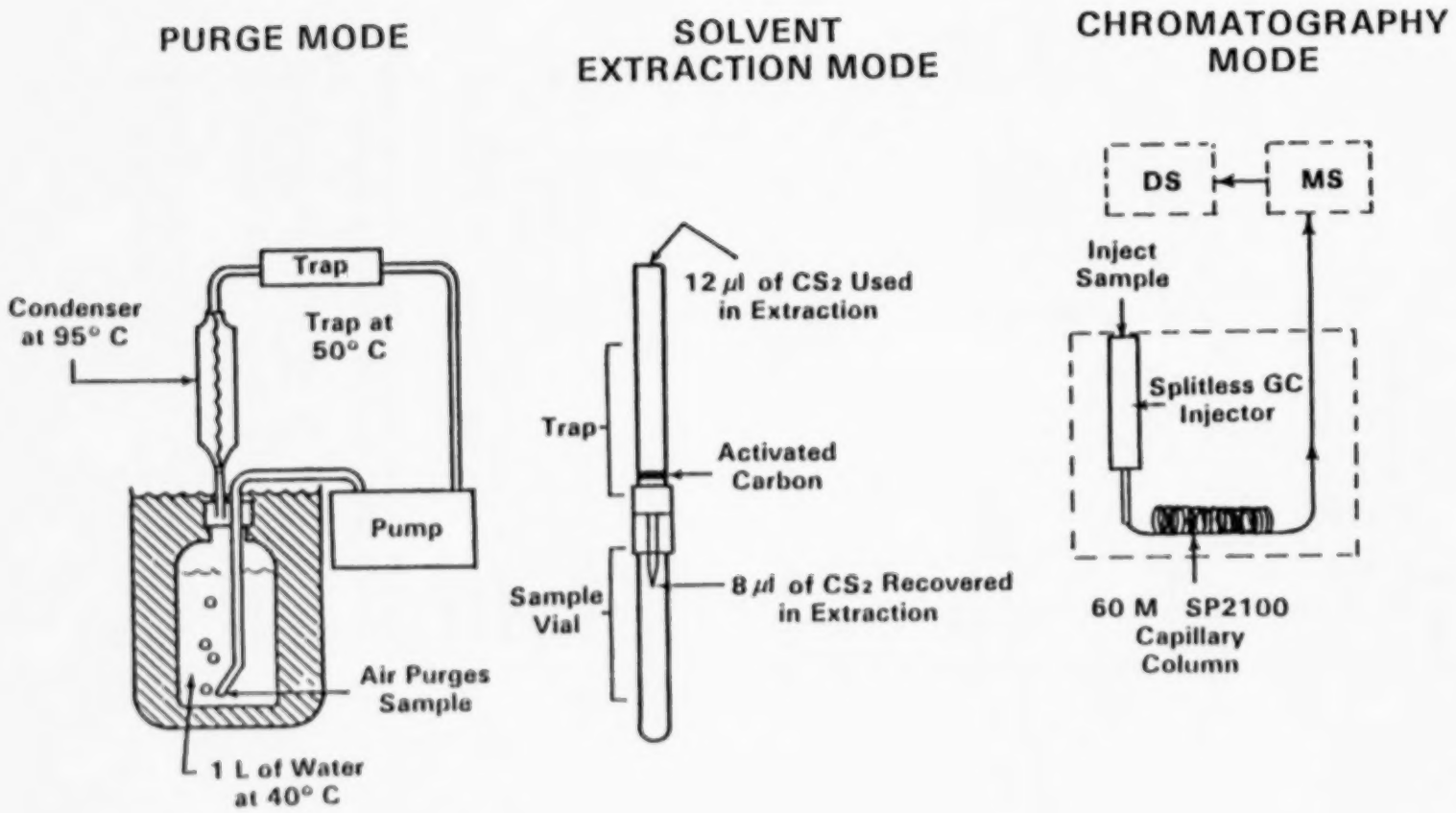
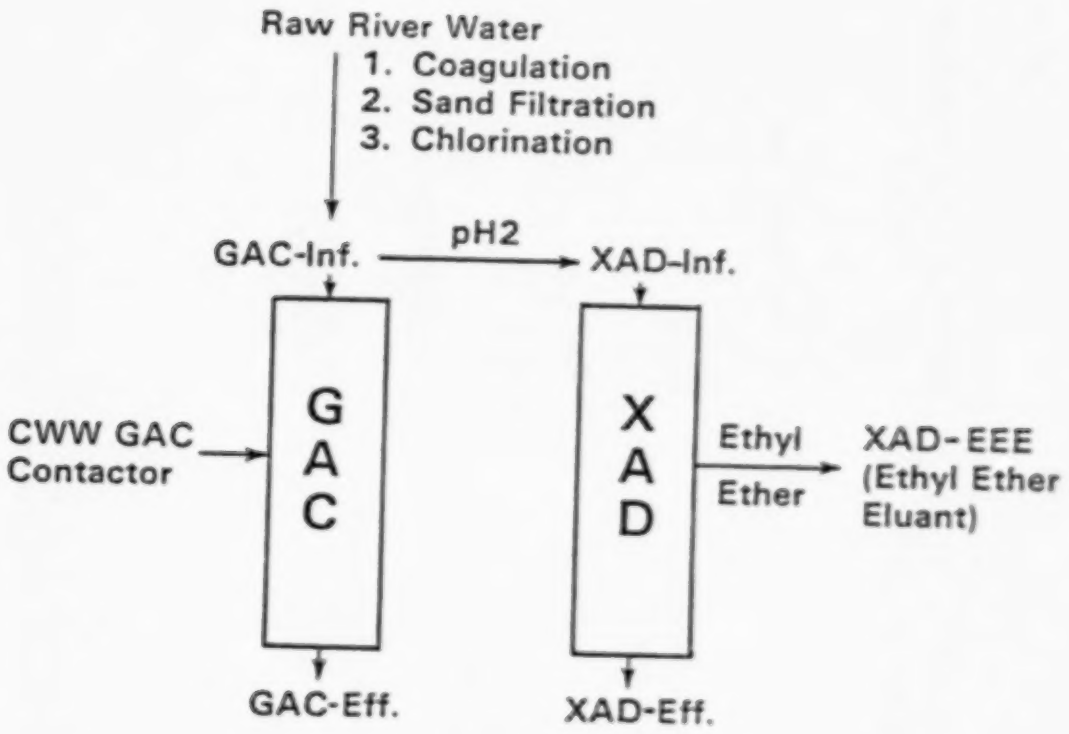


Figure 4 Fundamental Schematic of Grob CLSA Method as Modified by HERL-CI on August 1, 1980



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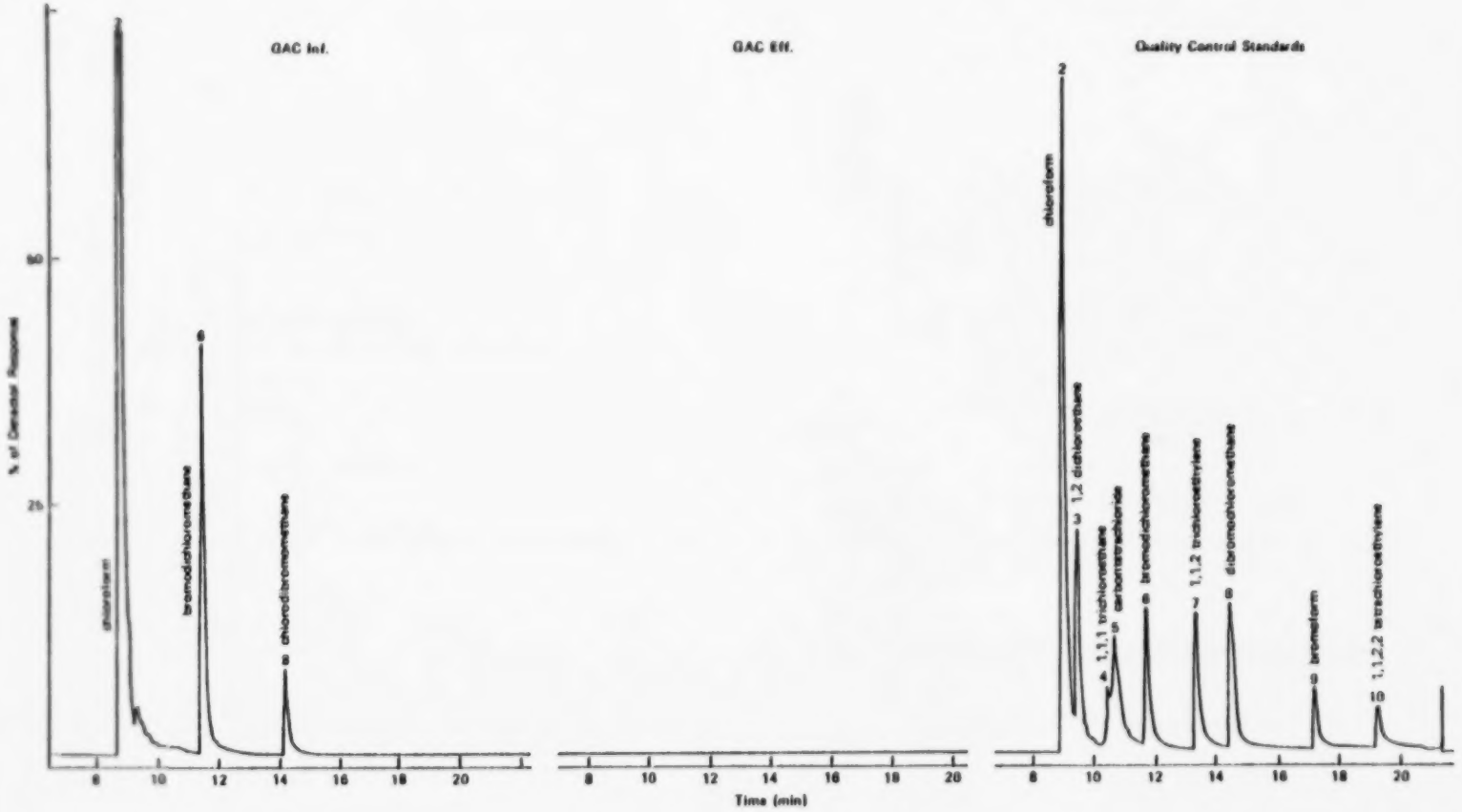
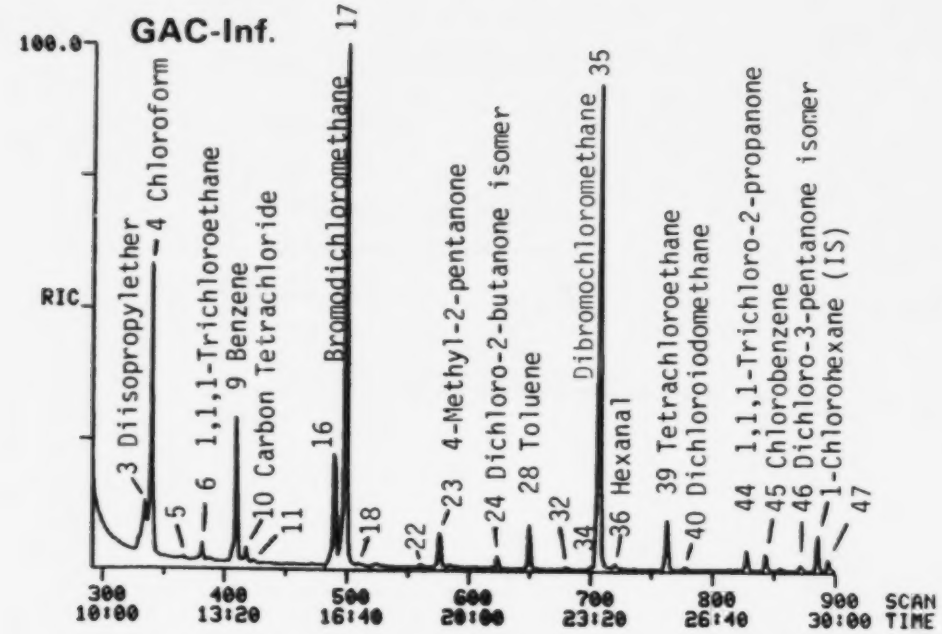


Figure 6 Chromatographic Results of Bellar P&T Analysis



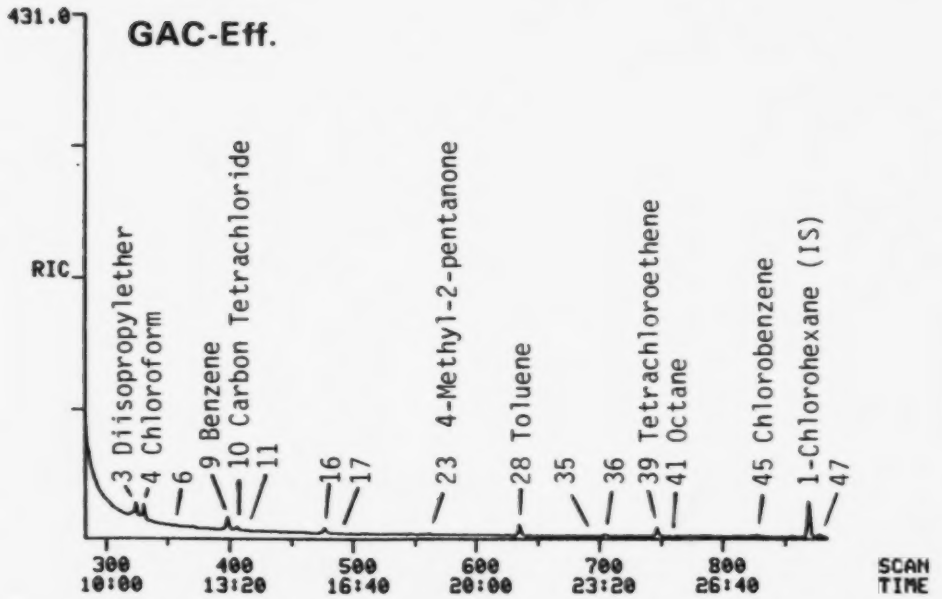


Figure 7

Chromatographic Results of GAC-Inf. and GAC-Eff. Water Using Grob CLSA, page 1 of 4.

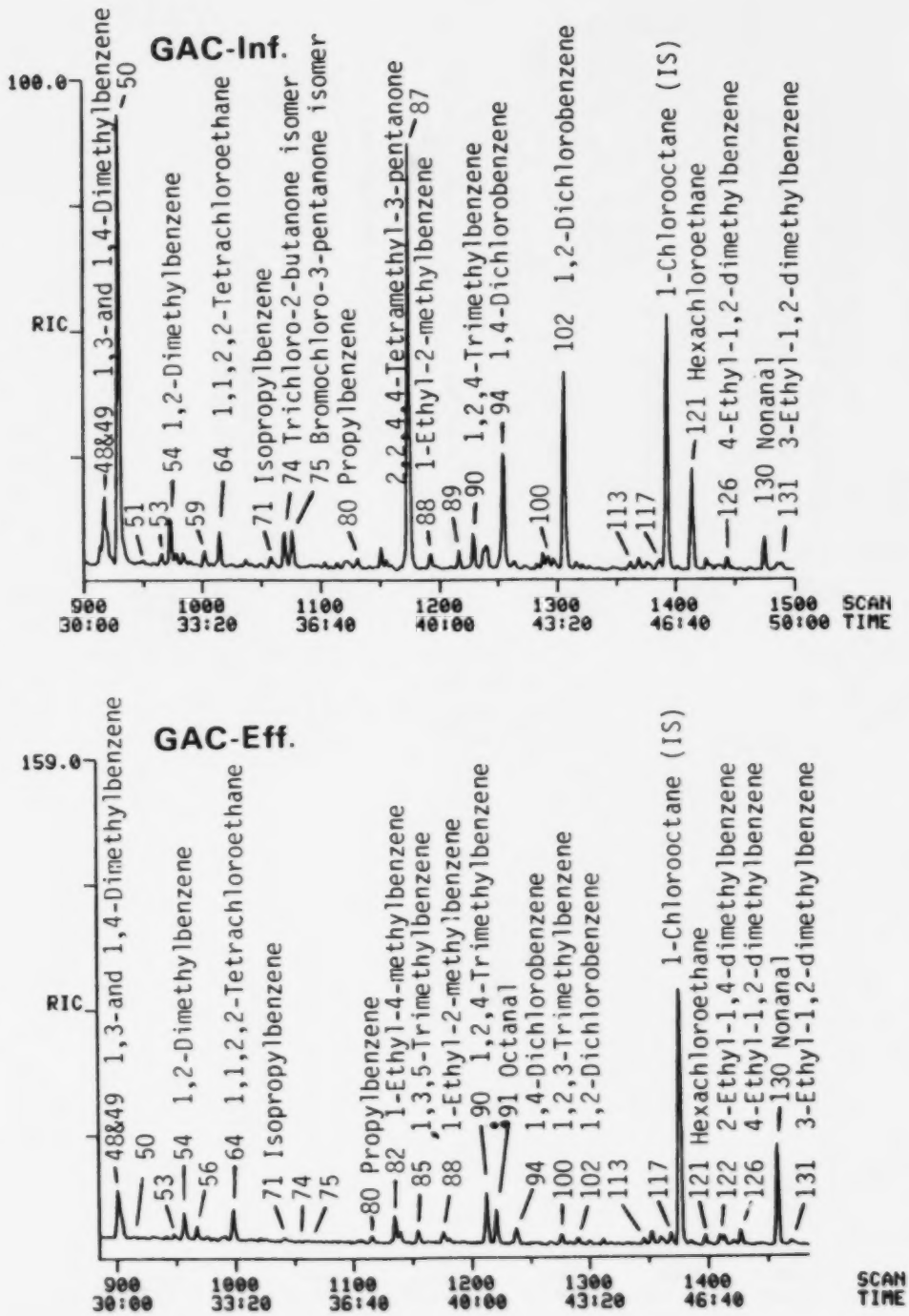


Figure 7

continued, page 2 of 4.

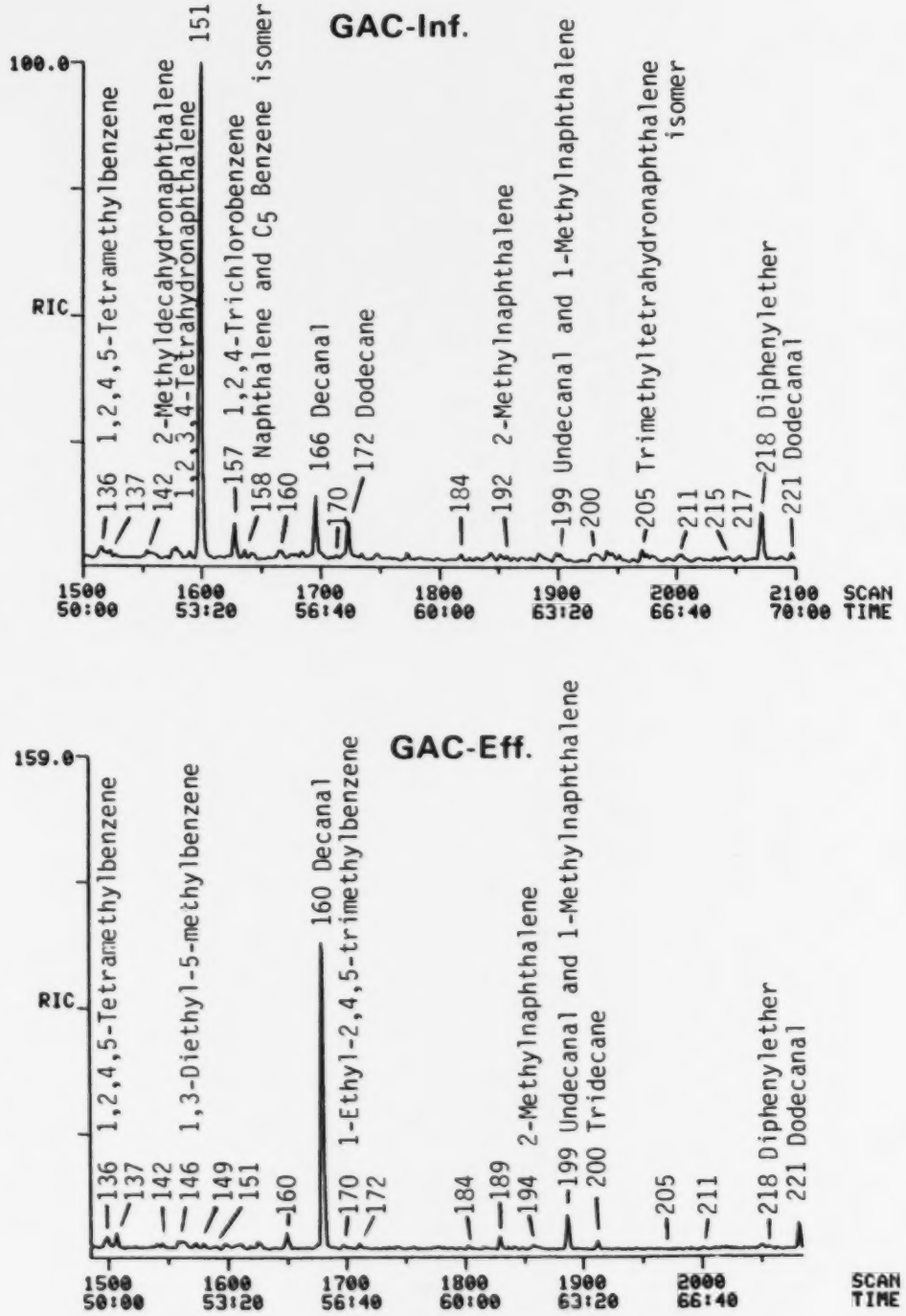


Figure 7

continued, page 3 of 4.

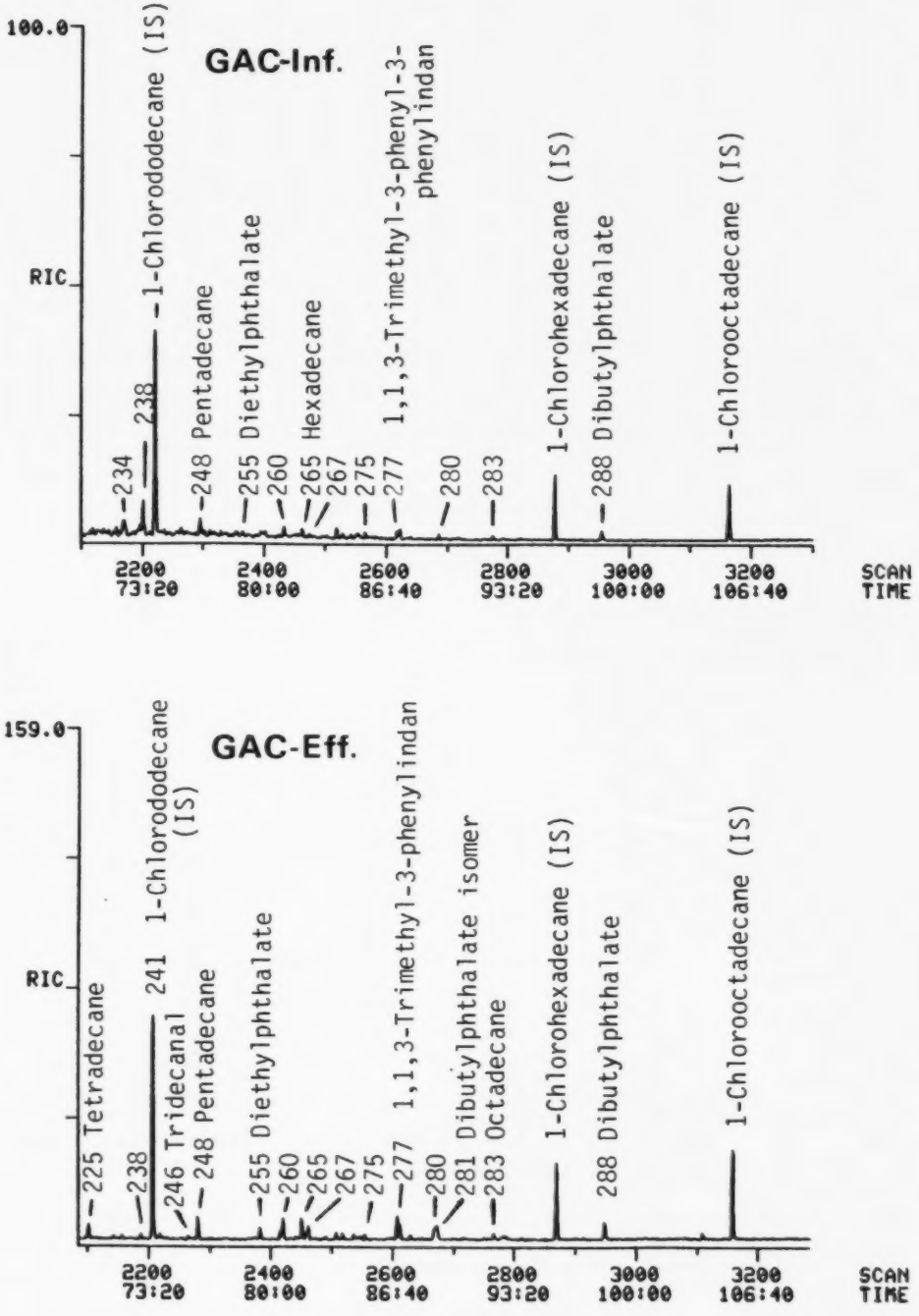


Figure 7

continued, page 4 of 4.

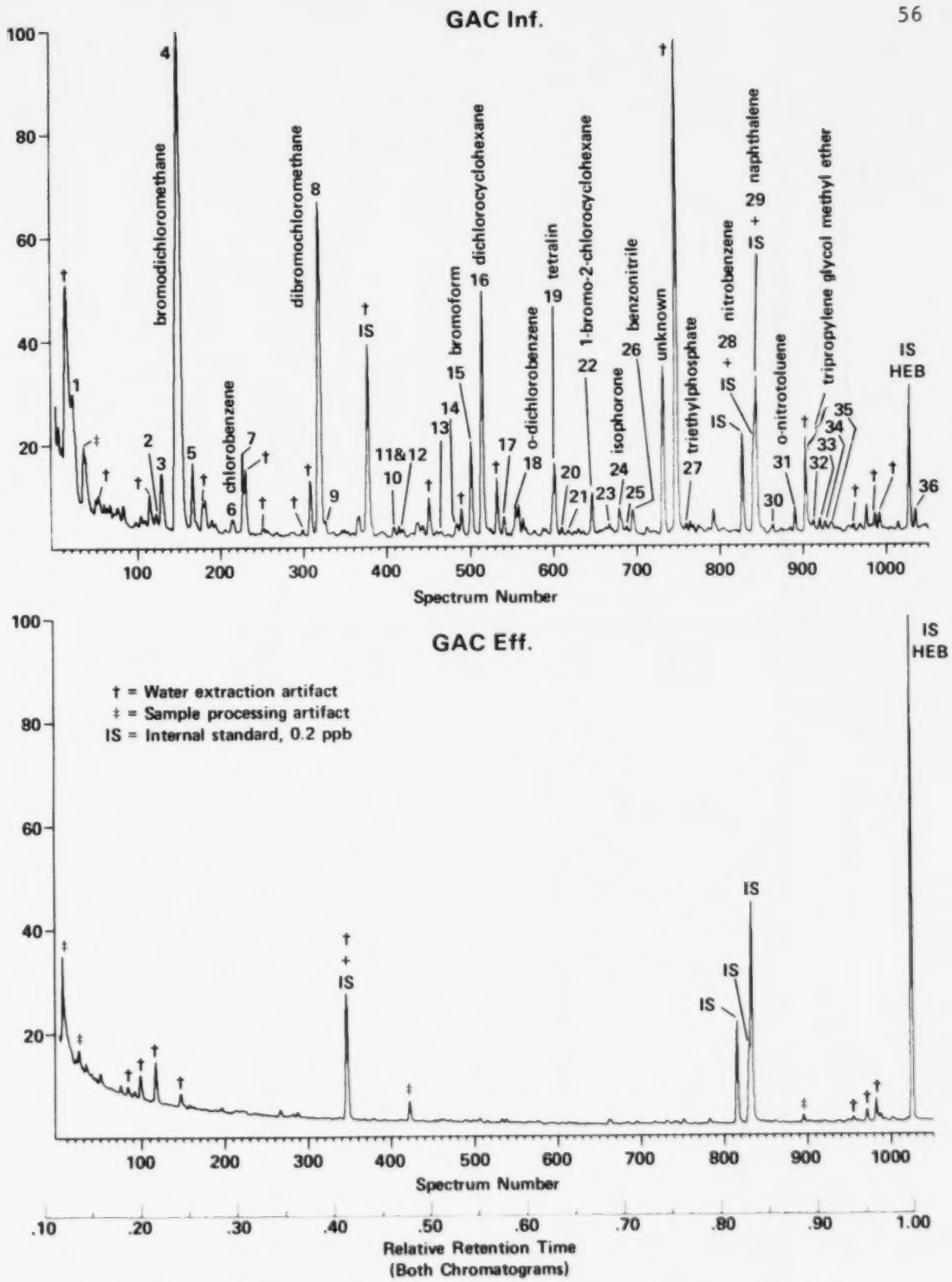


Figure 8 Chromatographic Results of BLLE Analysis of GAC-Inf. and GAC-EFF. Samples - Neutral Fraction, (page 1 of 2).

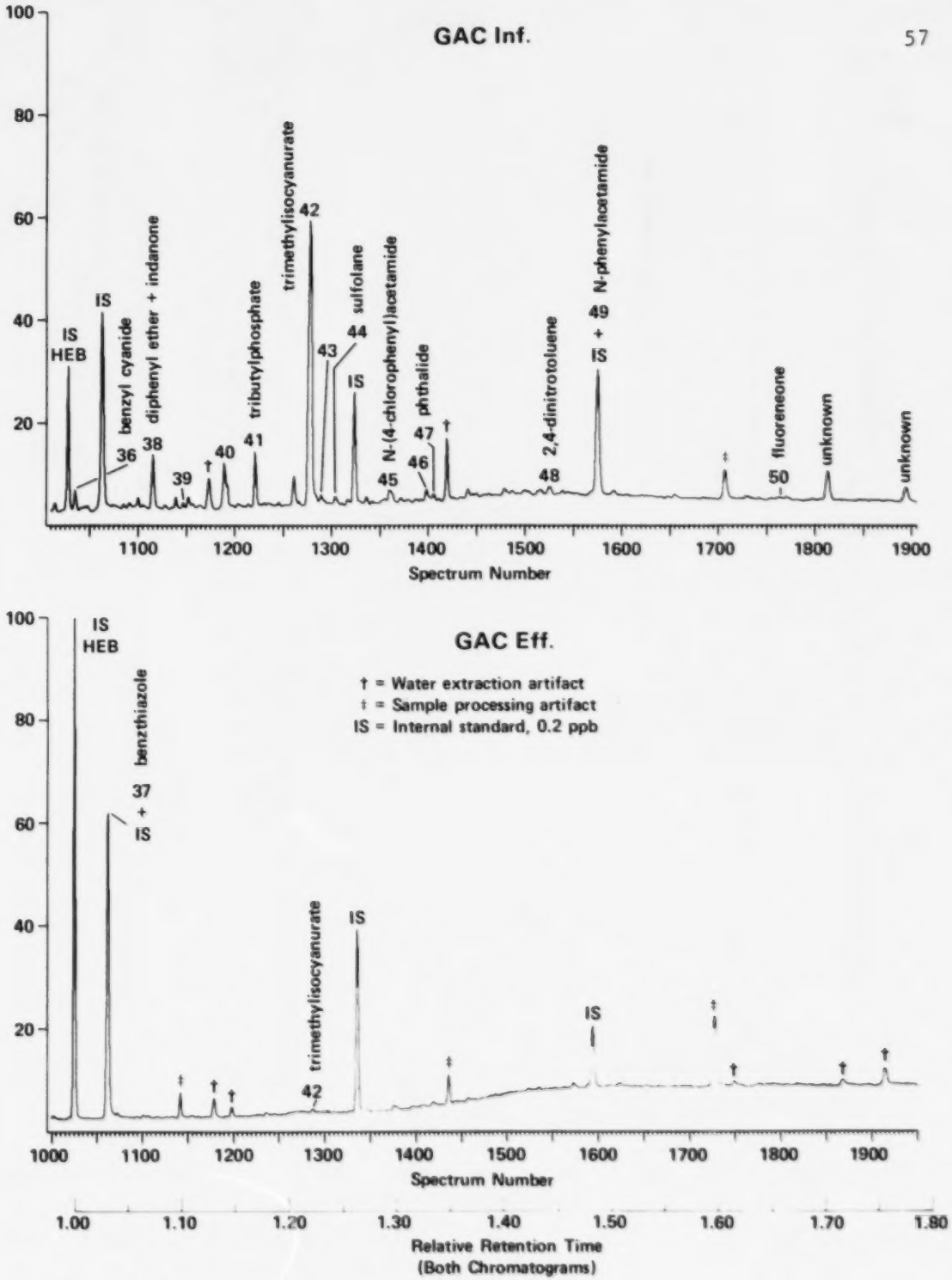


Figure 8 Continued, (page 2 of 2).

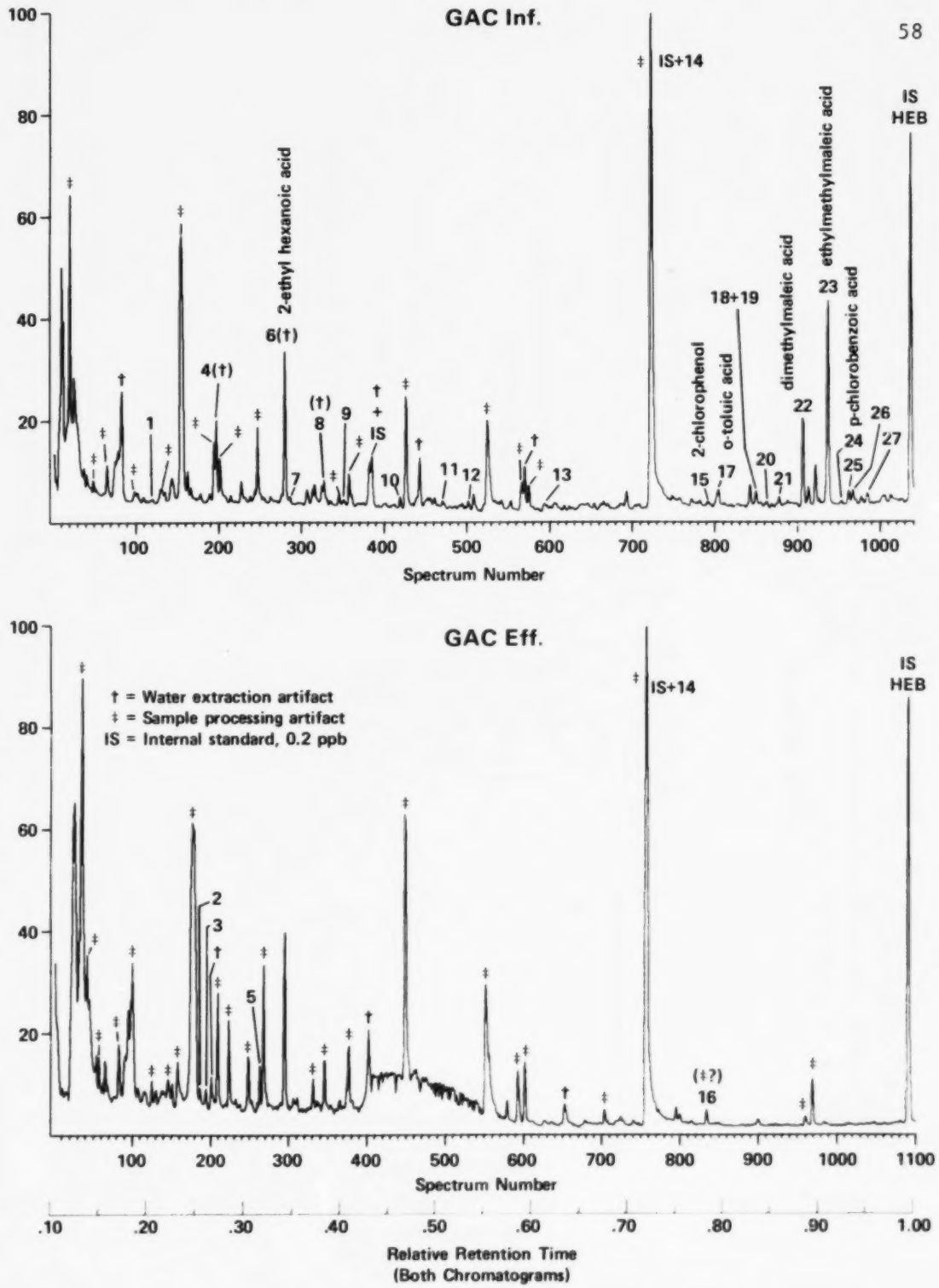


Figure 9 Chromatographic Results of BLLE Analysis of GAC-Inf. and GAC-EFF. Samples - Methylated Acid Fraction, (page 1 of 2).

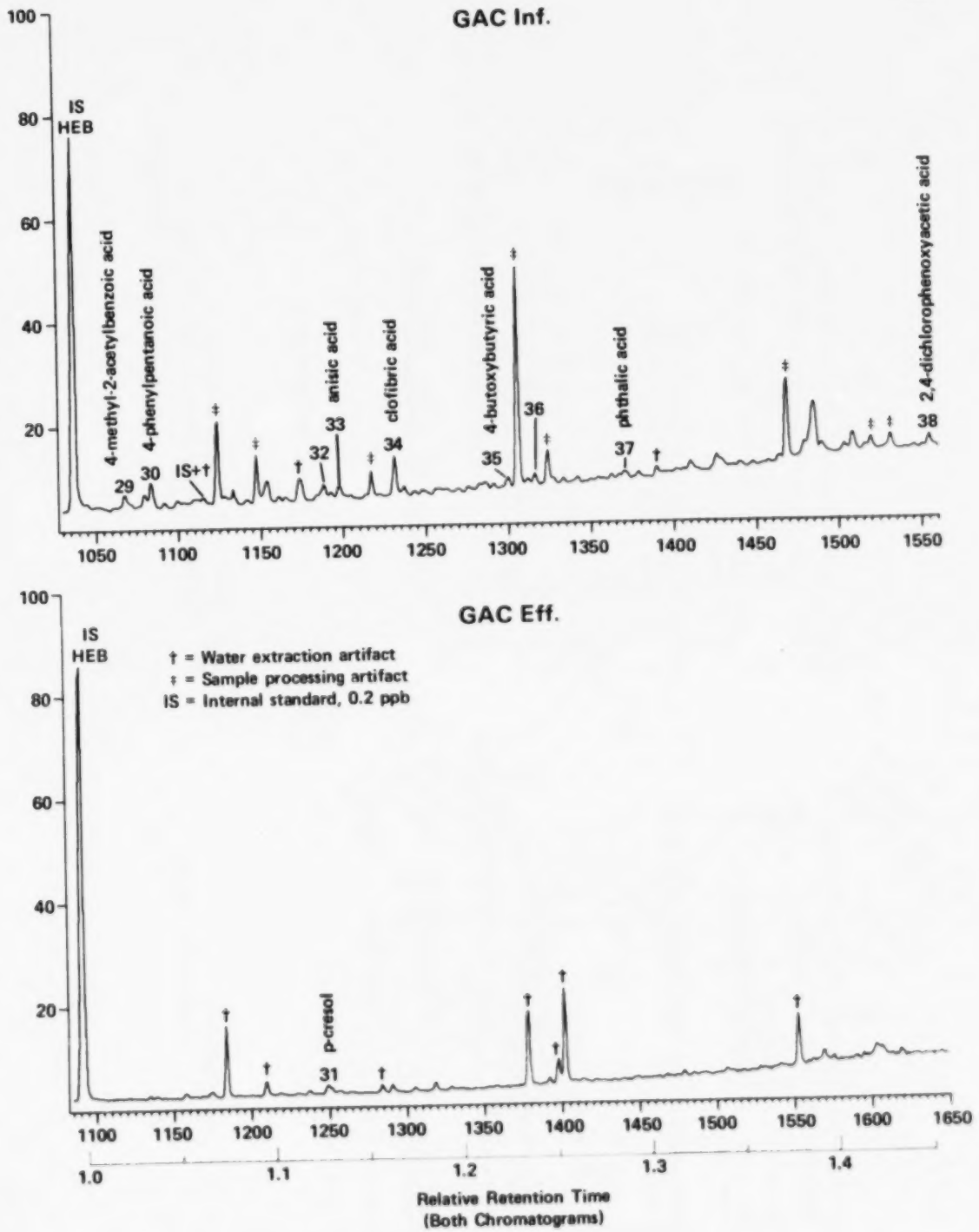


Figure 9 Continued, (page 2 of 2).

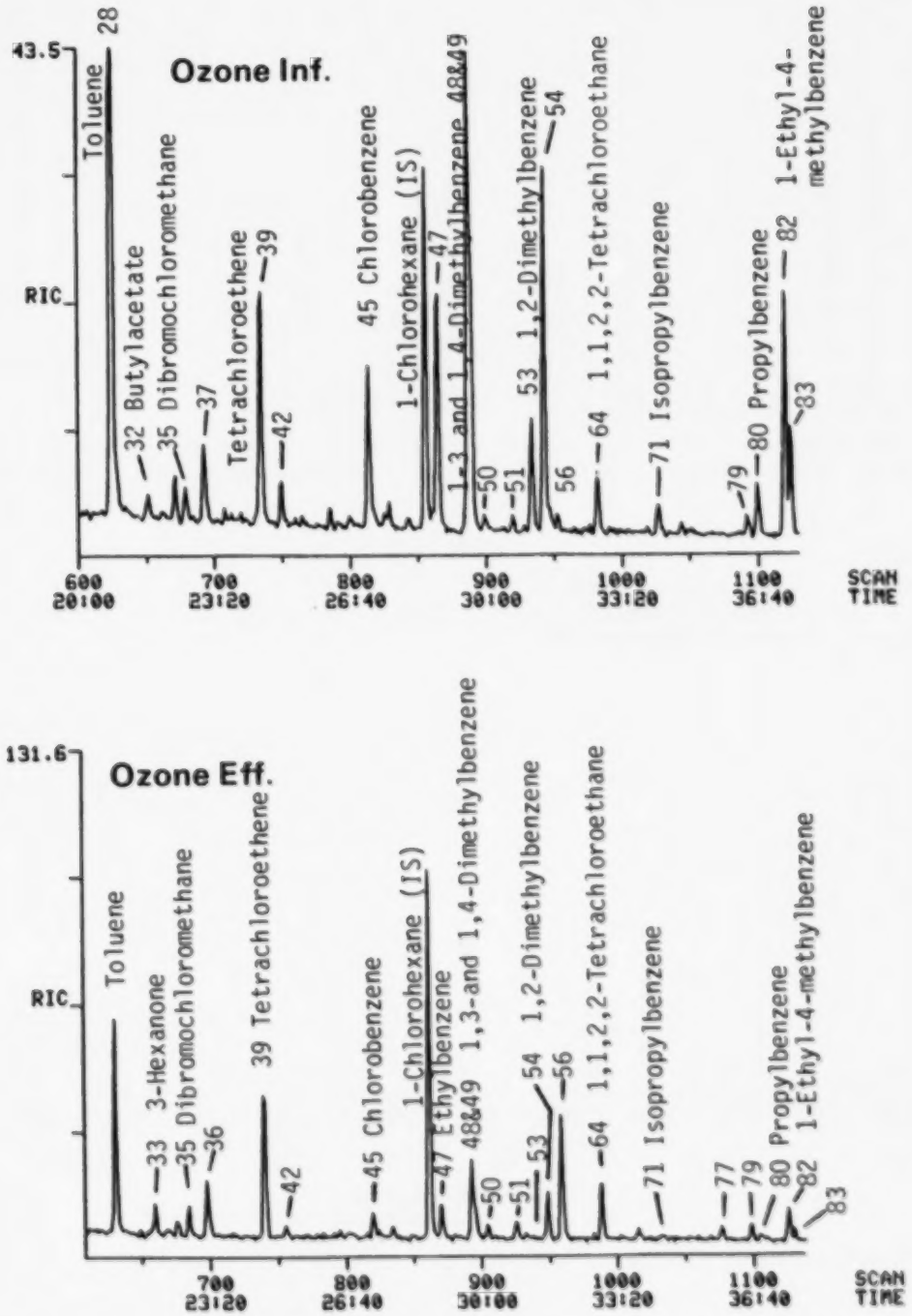


Figure 10 Chromatographic Grob CLSA Results of CWW Raw, Settled Water (Ozone-Inf.) Which was Treated With Ozone (Ozone-Eff.), page 1 of 2.

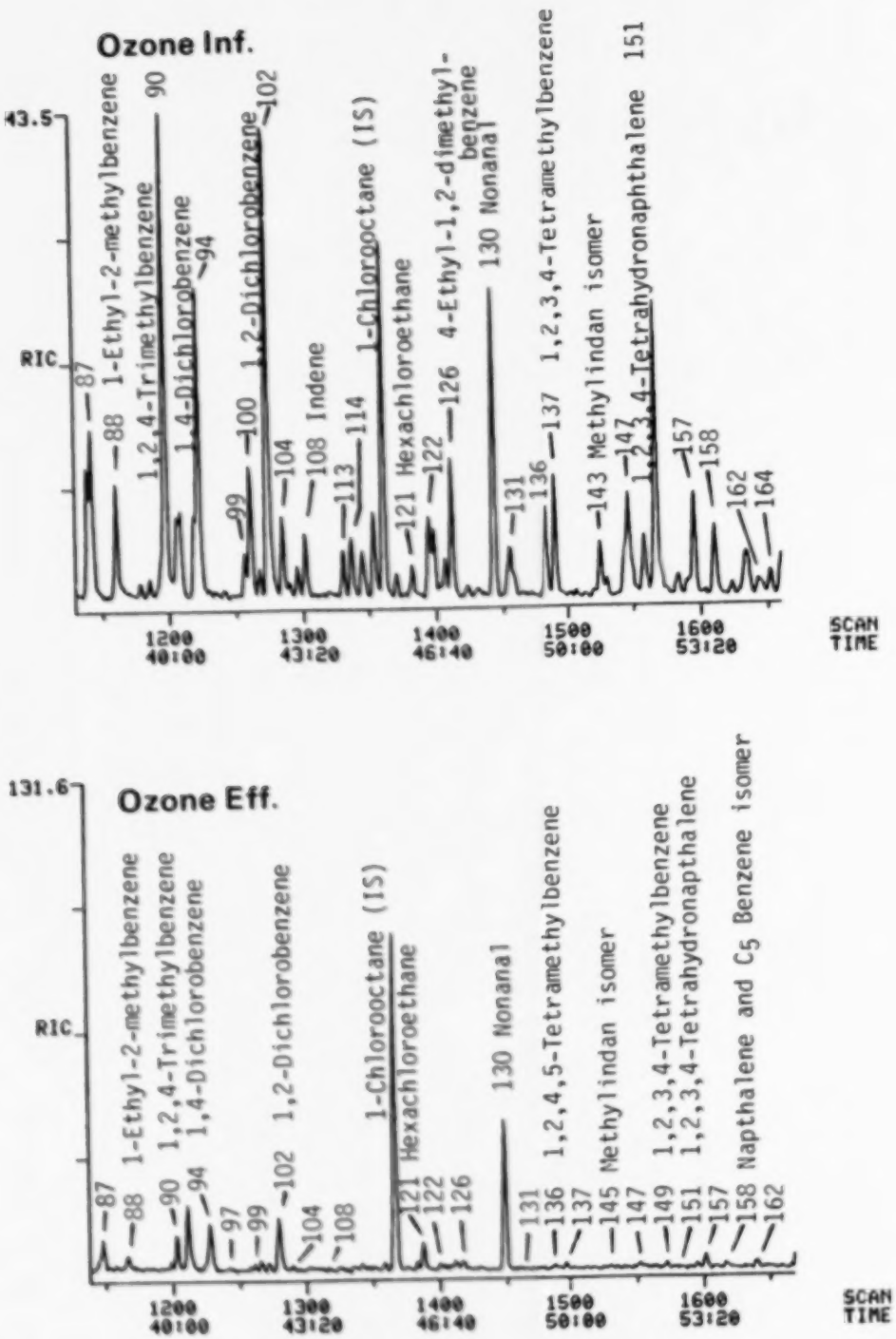


Figure 10

continued, page 2 of 2.

Table 1. Results of Bellar P&T Analysis

		GAC Contactor D Water[a]			GAC Contactor A Water[a]			
	Retention Time (min)	GAC-Inf. (µg/l)	GAC-Eff. (µg/l)	GAC-Eff. (% Removed[d])	GAC-Inf. (µg/l)	XAD-Inf. (µg/l)	XAD-Eff. (µg/l)	XAD-Eff. (% Removed[e])
1. Methylene Chloride	4.8	ND[b]	ND		ND	ND	ND	
2. Chloroform	8.9	56	ND	100	65	23	3.4	85
3. 1,2-Dichloroethane	9.5	ND	ND		ND	ND	ND	
4. 1,1,1-Trichloroethane	10.4	0.4	ND	100	1.9	ND	1.1	
5. Tetrachloromethane	10.7	ND	ND		ND	ND	TD	
6. Bromodichloromethane	11.7	18	ND	100	83	10.9	0.6	94
7. Trichloroethane	13.3	TD[c]	ND		TD	0.1	0.1	0
8. Chlorodibromomethane	14.4	5.8	ND	100	8.0	5.0	0.4	92
9. Bromoform	17.1	0.2	ND	100	ND	ND		
10. Tetrachloroethene	19.1	ND	ND		ND	ND	ND	

[a] Water samples described in figure 5

[b] ND = Not Detected

[c] TD = Trace Detected

[d] % Removed by GAC in Contactor D

[e] % Removed by XAD-2 Resin in Analytical Column (see figure 5)

Table 2. Results of Grob Capillary GC/MS/DS CLSA of GAC-Inf., GAC-Eff., XAD-Inf., and XAD-Eff. Samples

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
1. 2-Butanone[a]	.134								
2. 3-Methylpentane[a]	.136								
3. Diisopropylether	.146		141 RAU[f]	0 RAU	100	460 RAU	145 RAU	0 RAU	100
4. Chloroform	.149	S	10 ug/l	.60 ug/l	94	12 ug/l	5 ug/l	.40 ug/l	91
5. Methylcyclopentane	.161		NQ[g]					NQ	
6. 1,1,1-Trichloroethane	.167	S	8	1	88	4	2	0	100
7. 1-Chlorobutane[a]	.171								
8. 2-Pentanone	.175							NQ	
9. Benzene	.180	S	86	8	91	53	57	4	93
10. Carbon tetrachloride	.184	S	14	4	71	8	6	3	50
11. Cyclohexane	.186		4 RAU	0 RAU	100	8 RAU	7 RAU	0 RAU	100
12. Cy alkane isomer[a]	.198								
13. Cyclohexene[a]	.201								
14. Methylpropenoicacid, methylester isomer	.207							NQ	
15. 1,2-Dichloropropane	.208					2 RAU			
16. Trichloroethene	.215	S	57	3	95	6	7	2	71
17. Bromodichloromethane	.220	S	16 ug/l	.01 ug/l	100	13 ug/l	6.2 ug/l	.03 ug/l	100

Table 2., Continued, Page 2

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
18.	Methylpropenoicacid, methyl ester isomer	.230		2 RAU	0 RAU	100				
19.	Heptane	.233		5 RAU	0 RAU	100				
20.	1-Bromo-2-chloroethane[f]	.234								
21.	5,5-Dimethyl-2-hexene[f]	.240								
22.	Methylcyclohexane	.248		4 RAU	0 RAU	100	2 RAU	3 RAU	0 RAU	100
23.	4-Methyl-2-pentanone	.254		64 RAU	0 RAU	100	16 RAU	7 RAU	0 RAU	100
24.	Dichloromethylbutane isomer	.276		20 RAU	0 RAU	100		5 RAU	0 RAU	100
25.	4-Octanone[f]	.277								
26.	2,3,4-Trimethylpentane[f]	.284								
27.	2-Bromo-1-chloropropane[f]	.287								
28.	Toluene	.288	5	32	9	72	19	32	59	-84
29.	4-Methyl-2-pentanol[f]	.289								
30.	1,3-Dichloropropane[f]	.299								
31.	2-Methylthiophene[f]	.299	5	0	0		0	0	0	
32.	Butyl acetate isomer	.300		4 RAU	0 RAU	100				
33.	3-Hexanone[f]	.304								
34.	2-Ethyl-4-methyl-1,3-dioxolane	.310		5 RAU	0 RAU	100				

Table 2., Continued, Page 3

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
35. Dibromochloromethane	.313	S	6.2 ug/l	0	100	5.7 ug/l	2.9 ug/l	.01 ug/l	100
36. Hexanal	.319	S	6	4	33	0	6	0	100
37. Ethylmethyl-1,3-dioxolane isomer[a]	.320								
38. Trimethylcyclopentane isomer[a]	.331								
39. Tetrachloroethene	.338	S	18	3	83	14	20	3	85
40. Dichloroiodomethane	.345	S	9	0	100	47	15	0	100
41. Octane	.345			NQ					
42. Butyl acetate isomer[a]	.346								
43. Diethyltetrahydrofuran isomer[a]	.363								
44. 1,1,1-Trichloro-2-propanone	.369		34 RAU	0 RAU	100	1 RAU	8 RAU	0 RAU	100
45. Chlorobenzene	.375	S	14	2	86	10	14	1	93
46. Dichloro-3-pentanone isomer	.382		13 RAU	0 RAU	100		5 RAU	0 RAU	100
47. Ethylbenzene	.398	S	24	4	83	2	4	2	50
48. 1,3-Dimethylbenzene	.409	S	8	6	25	7	13	7	46
49. 1,4-Dimethylbenzene	.410	S	NQ	NQ		NQ	NQ	NQ	
50. Bromoform	.415	S	.51 ug/l	0	100	.66 ug/l	.38 ug/l	0	100
51. 3-Heptanone	.428					NQ			

Table 2., Continued, Page 4

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
52.	Trimethylcyclohexane isomer[a]	.430								
53.	Styrene	.430	S	0	1	-∞	2	2	0	100
54.	1,2-Dimethylbenzene	.434	S	5	3	40	4	6	3	50
55.	Dibutylether	.436		2 RAU	0 RAU	100	NQ	1 RAU	0 RAU	100
56.	Heptanal	.439		2 RAU	2 RAU	0	2 RAU	4 RAU	1 RAU	75
57.	Ethylmethylcyclohexane isomer	.442		NQ	NQ					
58.	Ethylmethylcyclohexane isomer[a]	.445								
59.	Bromochloroiodomethane + Bromo-trichloroethene	.448	S	3	0	100	6	5	0	100
60.	Dimethylpentanal isomer[a]	.448								
61.	1-Nonene	.449			NQ					
62.	Methylpropylcyclopentane isomer[a]	.450								
63.	1,2,3-Trichloropropane[a]	.451								
64.	1,1,2,2-Tetrachloroethane	.453	S	7	7	0	5	7	4	43
65.	Methoxybenzene or Phenylhydrazine[a]	.457								
66.	Trimethylcyclohexane isomer	.458			NQ					
67.	Benzonitrile[a]	.461								
68.	Trimethylcyclohexane isomer[a]	.463								

Table 2., Continued, Page 5

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
69. C_3 cyclohexane isomer[a]	.467								
70. C_4-C_5 Tetrahydrofuran isomer	.470					NQ			
71. Isopropylbenzene	.473	S	1	0	100	1	2	0	100
72. Methyloctahydropentalene isomer[a]	.474								
73. Isopropylcyclohexane[a]	.478								
74. Trichloro-2-butanone isomer	.479		9 RAU	0 RAU	100				
75. Bromochloro-3-pentanone isomer	.481		9 RAU	0 RAU	100	3 RAU	9 RAU	0	100
76. Ethylmethylcyclohexane isomer[a]	.488								
77. Propylcyclohexane	.490		NQ				NQ		
78. Chlorotoluene isomer	.498		NQ			NQ	1	0	100
79. 2-Ethylhexanal	.502		NQ						
80. Propylbenzene	.506	S	3	2	33	2	4	2	50
81. Octahydroindene	.511			NQ			NQ		
82. 1-Ethyl-4-methylbenzene	.515	S	2	3	-50	2	10	5	50
83. 1-Ethyl-3-methylbenzene	.517		2 RAU	3 RAU	-50	2 RAU	5 RAU	2 RAU	60
84. Dimethylcyclooctane or Tetramethyl hexene isomer	.519						2 RAU	0 RAU	100
85. 1,3,5-Trimethylbenzene	.524		0 RAU	3 RAU	-∞	1 RAU	7 RAU	2 RAU	71

Table 2., Continued, Page 6

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
86.	Pentachloroethane	.522	S	NQ						
87.	2,2,4,4-Tetramethyl-3-pentanone	.527		NQ			11	13	0	100
88.	1-Ethyl-2-methylbenzene	.534	S	1	1	0	2	2	1	50
89.	3-Ethyl-2,4-dimethylpentane	.546			NQ			2 RAU	0 RAU	100
90.	1,2,4-Trimethylbenzene	.551	S	3	4	-33	2	5	3	40
91.	Octanal	.555		5 RAU	7 RAU	-40	NQ	0 RAU	4 RAU	- ∞
92.	1,3-Dichlorobenzene	.556	S	5	0	100	23	36	0	100
93.	Dimethylheptanal isomer[a]	.561								
94.	1,4-Dichlorobenzene	.562	S	18	2	89	27	41	2	95
95.	Methylisopropylcyclohexane isomer[a]	.566								
96.	(2-Methylpropyl)benzene[a]	.567								
97.	(1-Methylpropyl)benzene[a]	.571								
98.	Decane	.576		NQ	NQ			NQ	NQ	
99.	1-Methyl-4-propyl-7-oxabicyclo [2.2.1]heptane	.577		4 RAU	0 RAU	100	3 RAU	2 RAU	0 RAU	100
100.	1,2,3-Trimethylbenzene	.580	S	1	1	0	1	2	1	50
101.	Methylisopropylbenzene isomer	.583			NQ			NQ	NQ	
102.	1,2-Dichlorobenzene+Methyliso-propylbenzene isomer	.585	S	17	1	94	24	33	1	97

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
103.	Trimethylcyclohexanone isomer[a]	.587								
104.	Indan	.590	S	1	0	100	0	1	0	100
105.	1,3,3-Trimethyl-2-oxabicyclo [2.2.2]octane	.593		NQ			NQ			
106.	(1-Methylpropyl)cyclohexane	.595		NQ	NQ			1 RAU	0 RAU	100
107.	Methylisopropylbenzene isomer[a]	.599								
108.	Indene	.599	S		NQ				NQ	
109.	Ethyldimethylbenzene isomer[a]	.599								
110.	Butylcyclohexane[a]	.604								
111.	2,2-Oxybis[1-chloro]propane[a]	.606								
112.	Pentylcyclopentane[a]	.609								
113.	1,3-Diethylbenzene	.611	S	1	1	0	1	1	0	100
114.	Methylpropylbenzene isomer	.614		3 RAU	3 RAU	0	1 RAU	5 RAU	2 RAU	60
115.	1,4-Diethylbenzene	.618	S	1	0	100	NQ	3	0	100
116.	n-Butylbenzene	.618	S	0	1	-∞	0	1	0	100
117.	5-Ethyl-1,3-dimethylbenzene	.621	S	0	1	-∞	1	2	1	50
118.	Decahydronaphthalene	.622		2 RAU	0 RAU	100				
119.	Methylpropylbenzene isomer	.629		NQ	NQ		NQ	NQ	NQ	

Table 2., Continued, Page 8

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
120. C_4 Cyclohexane isomer[a]	.632								
121. Hexachloroethane	.634	S	8	1	88	7	5	1	80
122. 2-Ethyl-1,4-dimethylbenzene	.640	S	2	1	50	NQ	4	0	100
123. 4-Ethyl-1,3-dimethylbenzene	.642	S	NQ	NQ		NQ	2	0	100
124. d-Fenchone[a]	.645	S	0	0		0	0	0	
125. Ethylstyrene isomer	.646		1 RAU	0 RAU	100	NQ	1 RAU	0 RAU	100
126. 4-Ethyl-1,2-dimethylbenzene	.648	S	1	1	0	1	2	1	50
127. 2-Ethyl-1,3-dimethylbenzene	.654	S	NQ						
128. Ethylisopropylbenzene isomer[a]	.657								
129. 1,1-Dimethylindan+C_4 cyclohexane isomer[a]	.659	S							
130. Nonanal	.662		8 RAU	24 RAU	-200	1 RAU	23 RAU	9 RAU	61
131. 3-Ethyl-1,2-dimethylbenzene	.668	S	1	1	0	0	1	0	100
132. C_5 Benzene isomer[a]	.669								
133. C_5 Benzene isomer[a]	.673								
134. C_5 Benzene isomer[a]	.675								
135. Undecane	.679			NQ			0 RAU	3 RAU	-∞
136. 1,2,4,5-Tetramethylbenzene	.681		4 RAU	3 RAU	25	NQ	8 RAU	0 RAU	100

Table 2., Continued, Page 9

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
137. 1,2,3,5-Tetramethylbenzene	.684	S	1	1	0	NQ	2	1	50
138. (3-Methylbutyl)benzene[a]	.687								
139. Dimethylindan isomer	.689					NQ	NQ	NQ	
140. 1,3,5-Trichlorobenzene	.691	S	0	0			NQ		
141. C_5 Benzene isomer[a]	.696								
142. 2-Methyldecahydronaphthalene	.698		1 RAU	0 RAU	100	1 RAU	3 RAU	0 RAU	100
143. Methylindan isomer	.699		NQ	NQ		NQ	5 RAU	0 RAU	100
144. C_5 Benzene isomer	.702			NQ		NQ			
145. Dimethylindan isomer	.705						NQ		
146. 1,3-Diethyl-5-methylbenzene	.707	S		NQ					
147. Methylindan or C_2 Styrene isomer	.709			NQ					
148. C_5 Benzene isomer[a]	.710								
149. 1,2,3,4-Tetramethylbenzene	.714	S	1	0	100	NQ	1	0	100
150. p-Isobutyltoluene	.718			NQ					
151. Tetrahydronaphthalene	.718	S	40	0	100	NQ	NQ		
152. Diethylmethylbenzene isomer	.721					NQ			
153. n-Pentylbenzene	.722	S		NQ					

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
154. C_5 Benzene isomer[a]	.722								
155. (1,1-Dimethylpropyl)benzene	.725			NQ					
156. C_5 Benzene isomer[a]	.729								
157. 1,2,4-Trichlorobenzene + C_5 Benzene isomer	.731	S	2	0	100	NQ	4	0	100
158. Naphthalene	.738	S	NQ	NQ		NQ	NQ	NQ	
159. Dimethylindan or Methylbutenyl-benzene isomer[a]	.744								
160. C_2 Indan isomer + a Siloxane	.748						7	0	100
161. C_2 Indan + C_6 Benzene isomers[a]	.749								
162. C_2 Indan isomer[a]	.753								
163. Ethyltrimethylbenzene isomer	.756			NQ					
164. C_2 Indan isomer	.756		1 RAU	4 RAU	-300	1			
165. 3-Ethyl-1,2,4-trimethylbenzene[a]	.760								
166. Decanal	.762		17 RAU	73 RAU	-330	8 RAU	39 RAU	17 RAU	56
167. 1,2,3-Trichlorobenzene	.763	S	NQ			1		NQ	
168. C_3 Indan isomer	.764		1 RAU	0 RAU	100	1 RAU	NQ		
169. C_6 Benzene isomer	.768					NQ			

Table 2., Continued, Page 11

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
170.	1-Ethyl-2,3,5-trimethylbenzene	.770			NQ					
171.	C_3 Indan or C_2 THN[b] isomer	.772		1 RAU	0 RAU	100	2 RAU	3 RAU	0 RAU	100
172.	Dodecane	.775		11 RAU	0 RAU	100		5 RAU	0 RAU	100
173.	C_5 Benzene isomer[a]	.778								
174.	Methyl THN isomer[a]	.780								
175.	Hexachloro-1,3-butadiene	.780	S	0	0		0	NQ	0	
176.	C_6 Benzene isomer	.786		2 RAU	0 RAU	100	NQ			
177.	C_6 Benzene isomer[a]	.788								
178.	Methyl THN isomer[a]	.790								
179.	C_5 Benzene isomer[a]	.792								
180.	C_6 Benzene + C_2 THN or C_3 Indan isomers	.797		2 RAU	0 RAU	100	NQ			
181.	C_6 Benzene isomer[a]	.799								
182.	C_6 Benzene isomer[a]	.802								
183.	Dimethylindan or Methyl THN isomer	.805		NQ	NQ					
184.	C_6 Benzene isomer	.808					NQ			
185.	Methyl THN isomer or 4,7-Dimethylindan	.818	S	1	0	100		2	0	100
186.	C_6 Benzene isomer[a]	.821								

Table 2., Continued, Page 12

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
187.	C_6 Benzene isomer	.824					NQ			
188.	C_7 Benzene isomer	.828					1 RAU			
189.	C_9-C_{12} Aldehyde isomer	.829		0 RAU	2 RAU	-∞				
190.	C_6 Benzene isomer	.833			NQ		1 RAU			
191.	Pentamethylbenzene	.835	S		NQ					
192.	C_6 Benzene isomer	.838			NQ					
193.	Dimethyl THN isomer[a]	.841								
194.	2-Methylnaphthalene	.842	S	NQ	NQ			NQ	NQ	
195.	C_3 Indan or C_2 THN isomer	.844					NQ	1 RAU	0 RAU	100
196.	C_3 Indan or C_2 THN isomer	.847					3 RAU	4 RAU	0 RAU	100
197.	C_3 Indan or C_2 THN isomer	.849					NQ			
198.	C_3 Indan or C_2 THN isomer[a]	.854								
199.	1-Methylnaphthalene + Undecanal	.855	S	NQ (1) RAU	NQ (8) RAU	(-700)		0	2	-∞
200.	Tridecane	.866			NQ			3 RAU	0 RAU	100
201.	Dimethyl THN isomer	.868						5 RAU	0 RAU	100
202.	C_6 Benzene isomer[a]	.871								
203.	Dimethyl THN isomer	.873						5 RAU	0 RAU	100

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
204.	Trimethylindan isomer	.875						4 RAU	0 RAU	100
205.	C_3 THN isomer	.887						6 RAU	0 RAU	100
206.	Dimethyl THN isomer[a]	.890								
207.	C_7 Benzene isomer	.890						4 RAU	0 RAU	100
208.	Ethyl THN or Trimethylindan isomer[a]	.892								
209.	Dimethyl THN isomer	.896						1 RAU	0 RAU	100
210.	Ethyl THN isomer[a]	.900								
211.	Trimethyl THN or C_4 Indan isomer	.901						7 RAU	0 RAU	100
212.	C_7 Benzene isomer[a]	.903								
213.	C_3 THN isomer + Siloxane	.907						NQ		
214.	1,1,-Biphenyl[a]	.914								
215.	Trimethyl THN isomer	.920						2 RAU	0 RAU	100
216.	C_7 Benzene isomer	.924						1 RAU	0 RAU	100
217.	Dimethyl THN isomer	.929						NQ		
218.	Diphenylether	.932		14 RAU	0 RAU	100		3 RAU	0 RAU	100
219.	C_2 Naphthalene isomer	.938			NQ			NQ		
220.	C_7 Benzene isomer	.940						1 RAU	0 RAU	100

Table 2., Continued, Page 14

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
221. Dodecanal	.943		0 RAU	5 RAU	- ∞		6 RAU	2 RAU	67
222. C_3 THN isomer	.946						1 RAU	0 RAU	100
223. C_3 THN isomer[a]	.950								
224. Dimethylnaphthalene isomer	.951			NQ					
225. Tetradecane	.953		0 RAU	3 RAU	- ∞		3 RAU	0 RAU	100
226. C_3 THN or C_4 Indan isomer[a]	.954								
227. C_5 THN or C_6 Indan isomer	.957						1 RAU	0 RAU	100
228. C_4 Indan or C_3 THN isomer	.958						3 RAU	0 RAU	100
229. C_4 Indan or C_3 THN isomer[a]	.962								
230. C_4 Indan or C_3 THN isomer[a]	.966								
231. Dimethylnaphthalene isomer[a]	.967								
232. C_4 Indan or C_3 THN isomer[a]	.971								
233. C_4 Indan or C_3 THN isomer	.974						1 RAU	0 RAU	100
234. Trimethyl THN isomer	.977		4 RAU	0 RAU	100		9 RAU	0 RAU	100
235. 5,9-Undecadien-2-one,6,10-dimethyl	.977			NQ					
236. C_3 THN or C_4 Indan isomer[a]	.982								
237. C_4 Dihydronaphthalene isomer	.984					1 RAU	3 RAU	0 RAU	100

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
238.	2,6-bis(1,1-Dimethylether)2,5-cyclohexadiene-1,4-dione	.991		10 RAU	0 RAU	100	NQ	24 RAU	0 RAU	100
239.	Trimethyldihydronaphthalene isomer	.992						1 RAU	0 RAU	100
240.	C_3 THN isomer	.997		NQ						
241.	1-Chlorododecane, I.S.	1.000	S	52	52		52	52	52	
242.	Diphenylmethane[a]	1.002								
243.	C_2 Biphenyl isomer[a]	1.010								
244.	C_2 Biphenyl isomer[a]	1.016								
245.	C_2 Biphenyl isomer[a]	1.020								
246.	Tridecanal	1.027			NQ			NQ	NQ	
247.	Hexylindan isomer[a]	1.029								
248.	Pentadecane	1.034		0 RAU	5 RAU	-∞		9 RAU	0 RAU	100
249.	C_9 Benzene isomer	1.037								
250.	Pentachlorobenzene[a]	1.037	S	0	0		0	0	0	
251.	Tetramethylindan isomer[a]	1.041								
252.	C_9 Benzene + C_3 THN or C_4 Indan isomers[a]	1.066								
253.	Trimethylnaphthalene isomer[a]	1.066								

Table 2.. Continued, Page 16

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
254.	C_2 Biphenyl isomer[a]	1.079								
255.	Diethylphthalate	1.080	S	1	0	100	1			
256.	C_2 Biphenyl isomer[a]	1.085								
257.	C_3 Biphenyl isomer	1.089						NQ		
258.	Dimethylbiphenyl isomer[a]	1.093								
259.	C_3 Biphenyl isomer	1.095		0 RAU	2 RAU	-∞		1 RAU	0 RAU	100
260.	2,2,4-Trimethylpenta-1,3-diol diisobutyrate	1.097		3 RAU	5 RAU	-67		1 RAU	0 RAU	100
261.	C_3 Biphenyl isomer[a]	1.100								
262.	C_3 Biphenyl isomer	1.103						1 RAU	0 RAU	100
263.	Tetradecanal	1.106							NQ	
264.	1,2-Diphenylhydrazine	1.108	S	NQ	NQ		.20	1	0	100
265.	Hexadecane	1.110		2 RAU	4 RAU	-100	1 RAU	3 RAU	0 RAU	100
266.	C_3 Biphenyl isomer	1.113		0 RAU	1 RAU	-∞	1 RAU	NQ RAU	NQ RAU	
267.	C_3 Biphenyl isomer	1.115		0 RAU	3 RAU	-∞		3 RAU	0 RAU	100
268.	Diethylbiphenyl isomer[a]	1.119								
269.	C_6 Indan isomer[a]	1.125								
270.	Phthalate isomer[a]	1.130								

	Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
271.	C_3 Biphenyl isomer	1.136			NQ			2 RAU	0 RAU	100
272.	2,5-bis(1,1-Dimethylpropyl)-2,5-cyclohexadiene-1,4-dione	1.141		NQ	NQ					
273.	C_5 Biphenyl isomer	1.146						7 RAU	0 RAU	100
274.	Diethylbiphenyl isomer	1.150					3 RAU			
275.	1-Chlorotetradecane	1.157		NQ	NQ		NQ	0 RAU	1 RAU	-∞
276.	C_4 Biphenyl isomer[a]	1.160								
277.	1,1,3-Trimethyl-3-phenylindan	1.181		2 RAU	6 RAU	-200	1 RAU	6 RAU	0 RAU	100
278.	Heptadecane	1.183		2 RAU	3 RAU	-50	1 RAU	3 RAU	1 RAU	67
279.	Diethylbiphenyl isomer[a]	1.187								
280.	Alkane isomer	1.191			NQ					
281.	Dibutylphthalate isomer	1.226			NQ					
282.	a Siloxane[a]	1.227								
283.	Octadecane	1.254		NQ	NQ		NQ	1 RAU	0 RAU	100
284.	Alkane isomer	1.263			NQ					
285.	Phthalate + a Siloxane[a]	1.274								
286.	1,1-bis(Ethylphenyl)ethane[a]	1.277								
287.	Nonadecane	1.321		NQ	NQ					NQ

Table 2., Continued, Page 18

Compound	RRT[c]	Quan. Method[d]	Contactor D Water[e] GAC-Inf.[e] (ng/l)	GAC-Eff.[e] (ng/l)	% Removal by GAC	Contactor A Water[e] GAC-Inf.[e] (ng/l)	XAD-Inf.[e] (ng/l)	XAD-Eff.[e] (ng/l)	% Removal by XAD
288. Dibutylphthalate isomer	1.335		NQ	NQ		NQ	NQ		NQ
289. 4-Phenylbicyclohexyl[a]	1.366								
290. Eicosane[a]	1.385								
291. Benzylbutylphthalate	1.563	S	NQ	NQ					NQ
292. Dioctylphthalate	1.683		NQ			NQ	NQ		NQ

[a]This compound was detected in CWW Contactor A GAC-Inf. water on February 20, 1980, but was not detected in any January 14 and 28, 1980 CWW samples. Compound is included in table 2 in order to provide additional relative retention time.

[b]THN = Tetrahydronapthalene

[c]RRT = Relative retention time, where RRT of chlorododecane = 1.000

[d]Method of Quantitation; All quantitation values reported in Table 2 are in ng/l unless otherwise noted. "S" indicates that a standard was purchased and the corresponding experimental relative response factor to that of chlorododecane, IS, was determined.

[e]See Figure 5 for an explanation of sample origin.

[f]RAU (Relative Area Unit) = $\frac{\text{Total Ion Current Area(UNK)}}{\text{Total Ion Current Area(IS)}} \times 52$

where: UNK = Unknown Compound
IS = Chlorododecane

[g]NQ = Organic was detected but was not quantified.

Table 3. Results of BLLE Analysis of GAC Inf. and GAC Eff. Samples[d] - Neutral Fraction, GAC Contactor D Water

Sequence Number[a]	Relative Retention Time[b]	Compound Name	Formula	Relative Amount Detected[c] GAC Inf.	GAC Eff.	Percent Removal
1	0.14	2-ethyl-4-methyl-1,3-dioxlane	$C_6H_{12}O_2$	75		100
2	0.23	4-methyl-3-penten-2-one	$C_6H_{10}O$	8		100
3	0.23	1-chloro-2,4-hexadiene	C_6H_9Cl	36		100
4	0.25	bromodichloromethane	$CHBrCl_2$	420		100
5	0.26	2,6-dimethyl-4-heptanone	$C_9H_{18}O$	44		100
6	0.30	chlorobenzene	C_6H_5Cl	9		100
7	0.31	1,1-dichlorocyclohexane	$C_6H_{10}Cl_2$	26		100
8	0.39	dibromochloromethane	$CHBr_2Cl$	229		100
9	0.40	cycloheptanone	$C_7H_{12}O$	7		100
10	0.46	2-methyl-2-cyclopenten-1-one	C_6H_8O	7		100
11	0.47	dichloroacetonitrile	C_2HNCl_2	2		100
12	0.47	1,1,3-trichloro-1-propene	$C_3H_3Cl_3$	3		100
13	0.51	m-dichlorobenzene	$C_6H_4Cl_2$	3		100
14	0.53	hexachloroethane	C_2Cl_6	9		100
15	0.54	bromoform	$CHBr_3$	75		100
16	0.55	1,2-dichlorocyclohexane	$C_6H_{10}Cl_2$	168		100
17	0.57	alcohol		14		100
18	0.59	o-dichlorobenzene	$C_6H_4Cl_2$	19		100
19	0.62	tetralin	$C_{10}H_{12}$	49		100
20	0.63	di(2-chloroethyl) ether	$C_4H_8OCl_2$	5		100
21	0.64	3-propylcyclopentene	C_8H_{14}	4		100
22	0.66	1-bromo-2-chlorocyclohexane	$C_6H_{10}ClBr$	29		100
23	0.68	fenchyl alcohol	$C_{10}H_{18}O$	5		100
24	0.69	isophorone	$C_9H_{14}O$	18		100
25	0.70	4-hydroxy-4-methylcyclohexanone	$C_7H_{12}O_2$	3		100
26	0.70	benzonitrile	C_7H_5N	16		100
27	0.76	triethyl phosphate	$C_6H_{15}O_4P$	6		100
28	0.83	nitrobenzene	$C_6H_5O_2N$	30		100
29	0.83	naphthalene	$C_{10}H_8$	8		100
30	0.85	2-phenyl-2-propanol	$C_9H_{12}O$	7		100
31	0.87	o-nitrotoluene	$C_7H_7O_2N$	18		100
32	0.89	tripropylene glycol methyl ether	$C_{10}H_{22}O_4$	5		100
33	0.89	" " " "	"	9		100
34	0.90	" " " "	"	7		100
35	0.90	" " " "	"	6		100
36	1.01	benzylcyanide	C_8H_7N	14		100
37	1.03	benzthiazole	C_7H_5NS		6	--
38	1.08	indanone plus phenyl ether	C_9H_8O $C_{12}H_{10}O$	37		100
39	1.10	dipropylene glycol 2-propenyl ether	$C_9H_{16}O_3$	5		100
40	1.14	3,4-dihydronaphthalen-1-one	$C_{10}H_{10}O$	31		100

Table 3. (Continued)

Sequence Number[a]	Relative Retention Time[b]	Compound Name	Formula	Relative Amount Detected[c] GAC Inf.	GAC Eff.	Percent Removal
41	1.17	tributyl phosphate	$C_{12}H_{27}O_4P$	38		100
42	1.22	trimethyl isocyanurate	$C_6H_9O_3N_3$	196	1	99
43	1.23	tetrahydro-1-naphthalenol	$C_{10}H_{12}O$	5		100
44	1.24	sulfolane	$C_4H_8O_2S$	5		100
45	1.29	N-(4-chlorophenyl)acetamide	C_8H_8ONCl	9		100
46	1.33	tetrahydro-trimethyl benzofuranone	$C_{11}H_{16}O_2$	8		100
47	1.33	phthalide	$C_8H_6O_2$	4		100
48	1.44	2,4-dinitrotoluene	$C_7H_6O_4N_2$	7		100
49	1.49	N-phenylacetamide	C_8H_9ON	42		100
50	1.66	fluorenone	$C_{13}H_8O$	1		100

[a] Numbers correspond to the GC peaks, as labeled in Figure 8.

[b] Relative to the internal standard, hexaethylbenzene.

[c] Expressed as a peak height percentage of the internal standard, hexaethylbenzene, 0.2 ppb.

[d] See Figure 5 for explanation of sample code names.

Table 4. Results of BLLE Analysis of GAC Inf. and GAC Eff. Samples[e] - Methylated Acid Fraction, GAC Contactor D Water

Sequence Number[a]	Relative Retention Time[b]	Compound Name[d]	Formula	Relative Amount Detected[c] GAC Inf.	GAC Eff.	Percent Removal
1	0.21	neoheptanoic acid, ME	$C_7H_{14}O_2$	1		100
2	0.25	1-butanol	$C_4H_{10}O_1$		3	-∞
3	0.26	dibutyl sulfite	$C_8H_{18}O_3S_1$		5	-∞
4	0.28	hexanoic acid, ME	$C_6H_{12}O_2$	20		100
5	0.31	3-methoxy-3-methyl-2-butanone	$C_6H_{12}O_2$		10	-∞
6	0.35	2-ethylhexanoic acid, ME	$C_9H_{18}O_2$	40		100
7	0.35	2-methyloctanoic acid, ME	$C_9H_{18}O_2$	1.5		100
8	0.38	heptanoic acid, ME	$C_7H_{14}O_2$	5		100
9	0.41	divinylmercury (artifact?)	C_4H_6Hg	1		--
10	0.46	dichloroacetic acid, ME	$C_2H_2O_2Cl_2$	3		100
11	0.51	m-dichlorobenzene	$C_6H_4Cl_2$	2		100
12	0.53	3,6-dimethyloctanoic acid, ME	$C_{10}H_{20}O_2$	2		100
13	0.61	1,3,5-trichlorobenzene	$C_6H_3Cl_3$	1.5		100
14	0.72	benzoic acid, ME	$C_7H_6O_2$	102	5	95
15	0.77	2-chlorophenol, ME	C_6H_5Cl	.05		100
16	0.78	a glycol ether			3.5	-∞
17	0.79	o-toluic acid, ME	$C_9H_8O_2$	5		100
18	0.82	m-toluic acid, ME	$C_9H_8O_2$	2		100
19	0.82	2-phenylpropanoic acid, ME	$C_9H_{10}O_2$	2		100
20	0.83	p-toluic acid, ME	$C_9H_8O_2$	1.5		100
21	0.85	phenylacetic acid, ME	$C_9H_8O_2$	2.5		100
22	0.87	dimethyl maleic acid, di-ME	$C_6H_8O_4$	24		100
23	0.90	ethylmethyl maleic acid, di-ME	$C_7H_{10}O_4$	55		100
24	0.91	p-chlorobenzoic acid, ME	$C_7H_5O_2Cl$	1		100
25	0.92	3(p-tolyl)propionic acid, ME	$C_{10}H_{12}O_2$	4		100
26	0.92	hydrocinnamic acid, ME	$C_9H_{10}O_2$	3.5		100
27	0.94	2,4-dimethylbenzoic acid, ME	$C_9H_{10}O_2$	3		100
28	0.96	3-phenylpentanoic acid, ME	$C_{11}H_{14}O_2$	2		100
29	1.03	4-methyl-2-acetylbenzoic acid, ME	$C_{10}H_{10}O_3$	3.5		100
30	1.04	4-phenylpentanoic acid, ME	$C_{11}H_{14}O_2$	7		100
31	1.13	p-cresol	$C_7H_8O_1$		2	-∞
32	1.13	a substituted naphthalene carboxylic acid, ME		4		100
33	1.14	anisic acid, ME	$C_8H_8O_3$	3		100
34	1.17	clofibric acid, ME	$C_{10}H_{11}O_3Cl$	10		100
35	1.23	4-butoxybutyric acid, ME	$C_8H_{14}O_3$	2		100
36	1.25	isomer of clofibric acid, ME	$C_{10}H_{11}O_3Cl$	2.5		100
37	1.30	phthalic acid, di-ME	$C_8H_6O_4$	1.5		100
38	1.47	2,4-dichlorophenoxyacetic acid, ME	$C_8H_6O_3Cl_2$	3		100

[a] Numbers correspond to the GC peaks, as labeled in Figure 9.

[b] Relative to the internal standard, hexaethylbenzene.

[c] Expressed as a peak height percentage of the internal standard, hexaethylbenzene, 0.2 ppb.

[d] ME indicates the compound was detected as the methyl ester or ether. The formula shown is that for the free acid.

[e] See Figure 5 for explanation of sample code names.

Table 5. Artifact Contaminants from XAD-2 Resin in the XAD-EEE Sample[a]

Compound[b]	Relative Amount[c]	Compound[b]	Relative Amount[c]
p-xylene	890	methyl (1-ethylpropyl) benzene	170
m-xylene	5170	4-ethyl styrene	5160
cumene	250	3-ethyl styrene	3280
o-xylene	5600	5-methyl indan	3040
a propyl benzene isomer	200	a methyl indan isomer	180
p-ethyltoluene	420	a dimethyl indan isomer	450
mesitylene	150	a methyl indan isomer	250
styrene	690	tetralin	360
1,2,4-trimethylbenzene	130	divinylbenzene isomer	790
m-diethylbenzene	1820	divinylbenzene isomer	630
p-diethylbenzene	1710	2-pentenylbenzene	240
o-diethylbenzene	720	1,1A,6,6A-tetrahydrocycloprop[A]indene	170
an ethyl cumene isomer	1000	methylbenzoate	1720
t-pentylbenzene	70	acetophenone	90
p-ethyl cumene	390	o-ethylbenzaldehyde	120
a propyl xylene isomer	1040	naphthalene	1390
3-phenylpentane	350	methyl m-ethylbenzoate	50
a methylindan isomer plus a C-6 benzene	1560	p-ethylacetophenone	50
a methyl styrene plus a C-5 benzene	80	2-methylnaphthalene	70
2-ethyl styrene	400	1-methylnaphthalene	40

[a] See Figure 5 for an explanation of sample code names.

[b] Listed in GC retention order.

[c] Expressed as the GC peak height percentage of the internal standard, hexaethylbenzene, added at the 0.2 ppb level.

Table 6. Results of Analysis of XAD Inf., XAD Eff., and XAD EEE Samples[a] -- Neutral Fraction, Contactor A Water

#	RRT[b]	Compound Name	XAD Inf. Relative Amount[c]	XAD Eff. Relative Amount[c]	XAD Eff. Percent Removal[d]	XAD EEE Relative Amount[c]	XAD EEE Percent Recovery[d]
1	0.15	bromodichloromethane	3		100		0
2	0.34	dibromochloromethane	27		100	14	52
3	0.39	p-methylpropylbenzene				2	∞
4	0.42	1,3-dimethyl-5-ethyl benzene				3	∞
5	0.44	(dichloromethyl)naphthalene	1		100		0
6	0.45	1,4-dimethyl-2-ethylbenzene				2	∞
7	0.45	1,3-dimethyl-4-ethylbenzene				2	∞
8	0.46	1,2-dimethyl-4-ethylbenzene				4	∞
9	0.48	ethyl dichloroacetate				1	∞
10	0.48	m-dichlorobenzene	1		100		0
11	0.52	p-dichlorobenzene	3		100		0
12	0.52	bromoform	12		100	8	75
13	0.57	o-dichlorobenzene	5		100	60	1200
14	0.62	di(2-chloroethyl) ether	1		100		0
15	0.68	1,1,2,3-tetrachloropropane	1		100		0
16	0.69	benzonitrile	3		100	2	66
17	0.72	methyl benzoate		4	- ∞	233	∞
18	0.76	ethyl benzoate				3	∞
19	0.80	o-ethylbenzaldehyde				13	∞
20	0.80	phenyl ethyl ketone	5		100		0
21	0.82	nitrobenzene	4		100		0
22	0.82	naphthalene	5	3	40	11	220
23	0.86	o-nitrotoluene	8		100	7	88
24	0.90	methyl m-ethylbenzoate				13	∞
25	0.92	methyl p-ethylbenzoate				5	∞
26	0.93	p-nitrotoluene	1.5		100		0
27	1.01	benzyl cyanide	4		100		0
28	1.02	2-chloroaniline	1		100		0
29	1.04	2,4-dichloro-1-nitrobenzene	.5		100		0
30	1.08	diphenyl ether	.5		100		0
31	1.11	hexachloropentane	15	.5	97		0
32	1.27	ethyl palmitate				2	∞
33	1.37	2,6-dinitrotoluene	5		100	3	60
34	1.44	2,4-dinitrotoluene	9		100	8	89

(a) See Figure 5 for an explanation of sample code names.

(b) RRT = relative retention time. Relative to the internal standard, hexaethylbenzene.

(c) Expressed as a peak height percentage of the internal standard, hexaethylbenzene. 0.2 ppb.

(d) Percent removal or recovery, relative to the original water: XAD Inf.

Table 7. Results of Analysis of XAD Inf., XAD Eff., and XAD EEE Samples[a]--Methylated Acid Fraction, Contactor A Water

#	RRT[b]	Compound Name[e]	XAD Inf. Relati e Amount[c]	XAD Eff. Relative Amount[c]	XAD Eff. Percent Removal[d]	XAD EEE Relative Amount[c]	XAD EEE Percent Recovery[d]
1	0.19	valeric acid, ME				7	∞
2	0.19	glycol ether				6	∞
3	0.27	formate				30	∞
4	0.30	an ether				30	∞
5	0.38	a fatty acid, ME				15	∞
6	0.41	1-chloro-2-propanol				9	∞
7	0.46	dichloroacetic acid, ME	15		100	16	106
8	0.48	2,2'-bis-1,3-dioxolane				9	∞
9	0.58	2,3,3-trichloroacrylic acid, ME				6	∞
10	0.61	an oxo-fatty acid, ME				2	∞
11	0.65	an oxo-fatty acid, ME				4	∞
12	0.65	an oxo-fatty acid, ME				4	∞
13	0.66	levulinic acid, ME	6		100		0
14	0.67	a 2,3-dimethyl fatty acid, ME				9	∞
15	0.69	capric acid, ME				19	∞
16	0.70	2,2-dichloroethanol	24		100		0
17	0.72	benzoic acid, ME		120	- ∞	200	∞
18	0.82	m-toluic acid, ME				3	∞
19	0.82	2-phenylpropionic acid, ME				4	∞
20	0.85	phenylacetic acid, ME	4		100	13	320
21	0.86	salicylic acid, ME	3		100	6	200
22	0.87	dimethylmaleic acid, di-ME	40	20	50	22	55
23	0.89	lauric acid, ME				74	∞
24	0.90	m-ethylbenzoic acid, ME				10	∞
25	0.90	ethylmethylmaleic acid, di-ME	68	30	44	96	140
26	0.91	tetrachlorobutenoic acid, ME				6	∞
27	0.92	p-ethylbenzoic acid, ME				13	∞
28	0.92	hydrocinnamic acid, ME	4		100	7	175
29	0.94	3,5-dimethylbenzoic acid, ME				7	∞
30	0.94	o-methylphenylacetic acid, ME	3		100		0
31	1.02	o-chloroaniline	3		100		0
32	1.02	4-methyl-2-acetylbenzoic acid, ME				5	∞
33	1.04	isomyristic acid, ME	4	1	25		0
34	1.04	α-phenyl-t-butyric acid, ME	2		100		0
35	1.09	suberic acid, di-ME				6	∞
36	1.10	phenoxyacetic acid, ME				11	∞
37	1.10	3-hydroxybenzisothiazole, ME		5	- ∞		
38	1.11	4(1,5-dimethyl-3-oxohexyl-cyclohexane carboxylic acid, ME				8	∞
39	1.13	isopentadecanoic acid, ME	14		100		0

Table 7. (Continued)

#	RRT[b]	Compound Name[e]	XAD Inf. Relative Amount[c]	XAD Eff. Relative Amount[c]	XAD Eff. Percent Removal[d]	XAD EEE Relative Amount[c]	XAD EEE Percent Recovery[d]
40	1.14	anisic acid, ME	5		100	8	160
41	1.17	clofibric acid, ME	11		100	9	82
42	1.18	azelaic acid, di-ME				30	∞
43	1.27	N-hydroxy phthalimide				6	∞
44	1.29	phthalic acid, di-ME				8	∞
45	1.31	anteisoheptadecanoic acid, ME	6		100		0
46	1.35	heptadecenoic acid, ME	16		100		0
47	1.46	linoleic acid, ME	28		100		0
48	1.47	2,4-dichlorophenoxyacetic acid, ME	6		100	5	83
49	1.49	a derivative of N,N-dimethyl urea				2	∞
50	1.48	4-ethoxyethyl aniline		10	- ∞		
51	1.49	1,4-benzothiazin-2-one	22		100		0
52	1.49	N-phenylacetamide		3	- ∞		

(a) See Figure 5 for an explanation of sample code names.

(b) RRT = relative retention time. Relative to the internal standard, hexaethylbenzene.

(c) Expressed as a peak height percentage of the internal standard, hexaethylbenzene, 0.2 ppb.

(d) Percent removal or recovery, relative to the original water: XAD Inf.

(e) ME = methyl ester or methyl ether.

Table 8. List of 215 Reference Compounds Which Are Measured In Each Grob CLSA Sample

	Compound	M.W.[a]	Formula	RRT[b]
1.	1,1-Dichloroethane	98	$C_2H_4Cl_2$	0.137
2.	Bromochloromethane	128	CH_2ClBr	0.153
3.	Chloroform	118	$CHCL_3$	0.155
4.	1,2-Dichloroethane	98	$C_2H_4Cl_2$	0.170
5.	1,1,1-Trichloroethane	132	$C_2H_3Cl_3$	0.173
6.	Benzene	78	C_6H_6	0.185
7.	Carbon tetrachloride	152	CCl_4	0.188
8.	Dibromomethane	172	CH_2Br_2	0.215
9.	Trichloroethene	130	C_2HCl_3	0.219
10.	Bromodichloromethane	162	$CHCl_2Br$	0.223
11.	N-Nitrosodimethylamine	74	$C_2H_6ON_2$	0.260
12.	Pyridine	79	C_5H_5N	0.260
13.	Bromotrichloromethane	196	CCl_3Br	0.284
14.	Toluene	92	C_7H_8	0.288
15.	2-Methylthiophene	98	C_5H_6S	0.295
16.	Dibromochloromethane	206	$CHClBR_2$	0.315
17.	Hexanal	100	$C_6H_{12}O$	0.323
18.	1,2,2-Trichloropropane	146	$C_3H_5Cl_3$	0.323
19.	Tetrachloroethene	164	C_2Cl_4	0.339
20.	Dichloroiodomethane	210	$CHCl_2I$	0.349
21.	1,1,2-Trichloropropane	146	$C_3H_5Cl_3$	0.367
22.	4-Hydroxy-4-methyl-2-pentanone	116	$C_6H_{12}O_2$	0.368
23.	Chlorobenzene	112	C_6H_5Cl	0.379
24.	Dibromodichloromethane	240	CCl_2Br_2	0.391
25.	1-Chlorohexane	120	$C_6H_{13}Cl$	0.396
26.	Ethylbenzene	106	C_8H_{10}	0.400
27.	m-Xylene	106	C_8H_{10}	0.411
28.	p-Xylene	106	C_8H_{10}	0.411
29.	Bromoform	250	$CHBr_3$	0.417
30.	Styrene	104	C_8H_8	0.425
31.	o-Xylene	106	C_8H_{10}	0.435
32.	1,2,3-Trichloropropane	146	$C_3H_5Cl_3$	0.442
33.	Bromotrichloroethene	208	C_2Cl_3Br	0.446
34.	1,1,2,2-Tetrachloroethane	166	$C_2H_2Cl_4$	0.446
35.	Isopropylbenzene	120	C_9H_{12}	0.475
36.	2-Chlorotoluene	126	C_7H_7Cl	0.499
37.	3-Chlorotoluene	126	C_7H_7Cl	0.501
38.	4-Chlorotoluene	126	C_7H_7Cl	0.504
39.	n-Propylbenzene	120	C_9H_{12}	0.507
40.	Bromocyclohexane	162	$C_6H_{11}Br$	0.512
41.	1-Ethyl-4-methylbenzene	120	C_9H_{12}	0.514
42.	1-Ethyl-3-methylbenzene	120	C_9H_{12}	0.515
43.	Pentachloroethane	200	C_2HCl_5	0.517
44.	Benzonitrile	103	C_7H_5N	0.518
45.	1,3,5-Trimethylbenzene	120	C_9H_{12}	0.523
46.	bis-(2-Chloroethyl)ether	142	$C_4H_8OCl_2$	0.525
47.	a-Methylstyrene	118	C_9H_{10}	0.530
48.	1-Ethyl-2-methylbenzene	120	C_9H_{12}	0.533
49.	(1,1-Dimethylethyl)benzene	134	$C_{10}H_{14}$	0.546
50.	Bromochloroiodomethane	254	$CHClBrI$	0.550

	Compound	M.W.[a]	Formula	RRT[b]
51.	1,2,4-Trimethylbenzene	120	C_9H_{12}	0.550
52.	1,3-Dichlorobenzene	146	$C_6H_4Cl_2$	0.556
53.	1,4-Dichlorobenzene	146	$C_6H_4Cl_2$	0.560
54.	a-Chlorotoluene	126	C_7H_7Cl	0.560
55.	(2-Methylpropyl)benzene	134	$C_{10}H_{14}$	0.567
56.	(1-Methylpropyl)benzene	134	$C_{10}H_{14}$	0.570
57.	1,2,3-Trimethylbenzene	120	C_9H_{12}	0.579
58.	1,2-Dichlorobenzene	146	$C_6H_4Cl_2$	0.585
59.	Indan	118	C_9H_{10}	0.589
60.	Indene	116	C_9H_8	0.597
61.	1-Phenylethanone	120	C_8H_8O	0.608
62.	1,3-Diethylbenzene	134	$C_{10}H_{14}$	0.610
63.	1,4-Diethylbenzene	134	$C_{10}H_{14}$	0.615
64.	n-Butylbenzene	134	$C_{10}H_{14}$	0.617
65.	2-Chloro-p-xylene	140	C_8H_9Cl	0.617
66.	N-Nitroso-di-n-propylamine	130	$C_6H_{14}ON_2$	0.618
67.	5-Ethyl-1,3-dimethylbenzene	134	$C_{10}H_{14}$	0.619
68.	2-Chlorostyrene	138	C_8H_7Cl	0.621
69.	1,2-Diethylbenzene	134	$C_{10}H_{14}$	0.621
70.	1-Chlorooctane	148	$C_8H_{17}Cl$	0.623
71.	3-Chlorostyrene	138	C_8H_7Cl	0.624
72.	4-Chlorostyrene	138	C_8H_7Cl	0.627
73.	Phenyl-2-butene	132	$C_{10}H_{12}$	0.627
74.	2,6-Dimethylstyrene	132	$C_{10}H_{12}$	0.633
75.	Hexachloroethane	234	C_2Cl_6	0.634
76.	2-Ethyl-1,4-dimethylbenzene	134	$C_{10}H_{14}$	0.639
77.	1,1-Dimethylindene	144	$C_{11}H_{12}$	0.642
78.	4-Ethyl-1,3-dimethylbenzene	134	$C_{10}H_{14}$	0.642
79.	d-Fenchone	152	$C_{10}H_{16}O$	0.644
80.	4-Chloro-1,2-dimethylbenzene	140	C_8H_9Cl	0.645
81.	4-Ethyl-1,2-dimethylbenzene	134	$C_{10}H_{14}$	0.647
82.	2-Ethyl-1,3-dimethylbenzene	134	$C_{10}H_{14}$	0.651
83.	(1,1-Dimethylpropyl)benzene	148	$C_{11}H_{16}$	0.653
84.	4-Ethylstyrene	132	$C_{10}H_{12}$	0.653
85.	1,1-Dimethylindan	146	$C_{11}H_{14}$	0.662
86.	3-Ethyl-1,2-dimethylbenzene	134	$C_{10}H_{14}$	0.666
87.	a-Chloro-m-xylene	140	C_8H_9Cl	0.667
88.	Isophorone	138	$C_9H_{14}O$	0.667
89.	a-Chloro-o-xylene	140	C_8H_9Cl	0.670
90.	a-Chloro-p-xylene	140	C_8H_9Cl	0.670
91.	2,4-Dichlorotoluene	160	$C_7H_6Cl_2$	0.675
92.	2,5-Dichlorotoluene	160	$C_7H_6Cl_2$	0.676
93.	2,6-Dichlorotoluene	160	$C_6H_6Cl_2$	0.679
94.	1,1,2,3,3-Pentachloropropane	214	$C_3H_3Cl_5$	0.679
95.	5-Isopropyl-1,3-dimethylbenzene	148	$C_{11}H_{16}$	0.680
96.	o-Chloroaniline	127	C_6H_6NCl	0.681
97.	1,2,3,5-Tetramethylbenzene	134	$C_{10}H_{14}$	0.681
98.	1,3,5-Trichlorobenzene	180	$C_6H_3Cl_3$	0.688
99.	d-Camphor	152	$C_{10}H_{16}O$	0.694
100.	Isoborneol	154	$C_{10}H_{18}O$	0.696
101.	p-Methylphenol	108	C_7H_8O	0.699
102.	3,4-Dichlorotoluene	160	$C_7H_6Cl_2$	0.702

	Compound	M.W.[a]	Formula	RRT[b]
103.	1,3-Diethyl-5-methylbenzene	148	$C_{11}H_{16}$	0.704
104.	bis(2-Chloroethoxy)methane	172	$C_5H_{10}O_2Cl_2$	0.706
105.	Menthone	154	$C_{10}H_{18}O$	0.706
106.	1,2,3,4-Tetramethylbenzene	134	$C_{10}H_{14}$	0.713
107.	1,2-Dihydronaphthalene	130	$C_{10}H_{10}$	0.717
108.	1,3-Diisopropylbenzene	162	$C_{12}H_{18}$	0.717
109.	1,2,3,4-Tetrahydronaphthalene	132	$C_{10}H_{12}$	0.718
110.	n-Pentylbenzene	148	$C_{11}H_{16}$	0.720
111.	Borneol	154	$C_{11}H_{18}O$	0.726
112.	1,2,4-Trichlorobenzene	180	$C_6H_3Cl_3$	0.729
113.	a,2-Dichlorotoluene	160	$C_7H_6Cl_2$	0.730
114.	1,4-Diisopropylbenzene	162	$C_{12}H_{18}$	0.734
115.	Naphthalene	128	$C_{10}H_8$	0.737
116.	1-tert-Butyl-3,5-dimethylbenzene	162	$C_{12}H_{18}$	0.741
117.	a,3-Dichlorotoluene	160	$C_7H_6Cl_2$	0.742
118.	a,4-Dichlorotoluene	160	$C_7H_6Cl_2$	0.743
119.	m-Chloroaniline	127	C_6H_6NCl	0.751
120.	p-Chloroaniline	127	C_6H_6NCl	0.755
121.	1,2,3-Trichlorobenzene	180	$C_6H_3Cl_3$	0.761
122.	2-Methylpentylbenzene	162	$C_{12}H_{18}$	0.766
123.	2,6-Dichlorostyrene	172	$C_8H_6Cl_2$	0.769
124.	a,a,a-Trichlorotoluene	194	$C_7H_5Cl_3$	0.773
125.	2,5-Dichlorostyrene	172	$C_8H_6Cl_2$	0.777
126.	Hexachloro-1,3-butadiene	258	C_4Cl_6	0.779
127.	1,3,5-Triethylbenzene	162	$C_{12}H_{18}$	0.782
128.	2,5-Dichloro-p-xylene	174	$C_8H_8Cl_2$	0.784
129.	3,4-Dichlorostyrene	172	$C_8H_6Cl_2$	0.804
130.	4,7-Dimethylindan	146	$C_{11}H_{14}$	0.817
131.	n-Hexylbenzene	162	$C_{12}H_{18}$	0.817
132.	Pentamethylbenzene	148	$C_{11}H_{16}$	0.834
133.	2-Methylnaphthalene	142	$C_{11}H_{10}$	0.839
134.	5-Methyltetrahydronaphthalene	146	$C_{11}H_{14}$	0.840
135.	2,4,5-Trichlorotoluene	194	$C_7H_5Cl_3$	0.841
136.	2,3,6-Trichlorotoluene	194	$C_7H_5Cl_3$	0.851
137.	1-Methylnaphthalene	142	$C_{11}H_{10}$	0.855
138.	a,a'-Dichloro-o-xylene	174	$C_8H_8Cl_2$	0.859
139.	Cyclohexylbenzene	160	$C_{12}H_{16}$	0.867
140.	2,6-Dimethyltetrahydro-naphthalene	160	$C_{12}H_{16}$	0.867
141.	2,5-Dichloroaniline	161	$C_6H_5NCl_2$	0.868
142.	1,2,3,5-Tetrachlorobenzene	214	$C_6H_2Cl_4$	0.870
143.	1,2,4,5-Tetrachlorobenzene	214	$C_6H_2Cl_4$	0.870
144.	a,2,4-Trichlorotoluene	194	$C_7H_5Cl_3$	0.877
145.	a,2,6-Trichlorotoluene	194	$C_7H_5Cl_3$	0.880
146.	Hexachloro-1,3-cyclopentadiene	370	C_5Cl_6	0.884
147.	1,8-Dimethyltetrahydro-naphthalene	160	$C_{12}H_{16}$	0.886
148.	a,a'-Dichloro-m-xylene	174	$C_8H_8Cl_2$	0.896
149.	a,a'-Dichloro-p-xylene	174	$C_8H_8Cl_2$	0.904
150.	Butylbenzoate	178	$C_{11}H_{14}O_2$	0.908

	Compound	M.W.[a]	Formula	RRT[b]
151.	2-Chloronaphthalene	162	$C_{10}H_7Cl$	0.909
152.	n-Heptylbenzene	176	$C_{13}H_{20}$	0.909
153.	1,2,3,4-Tetrachlorobenzene	214	$C_6H_2Cl_4$	0.910
154.	a,3,4-Trichlorotoluene	194	$C_7H_5Cl_3$	0.914
155.	2-Ethylnaphthalene	156	$C_{12}H_{12}$	0.928
156.	5,7-Dimethyltetrahydro-naphthalene	160	$C_{12}H_{16}$	0.929
157.	1-Ethylnaphthalene	156	$C_{12}H_{12}$	0.929
158.	2-Methylbiphenyl	168	$C_{13}H_{12}$	0.932
159.	1-Phenyl-1-cyclohexene	158	$C_{12}H_{14}$	0.933
160.	2,4,6-Trichloroaniline	195	$C_6H_4NCl_3$	0.935
161.	2,6-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.938
162.	1,3-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.950
163.	1,6-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.953
164.	Diphenylmethane	168	$C_{13}H_{12}$	0.955
165.	1,4-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.965
166.	2,3-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.966
167.	2-Methoxynaphthalene	158	$C_{11}H_{10}O$	0.970
168.	1,2-Dimethylnaphthalene	156	$C_{12}H_{12}$	0.977
169.	2-Isopropylnaphthalene	170	$C_{13}H_{14}$	0.981
170.	Hexamethylbenzene	162	$C_{12}H_{18}$	0.982
171.	n-Octylbenzene	190	$C_{14}H_{22}$	0.996
172.	Acenaphthene	154	$C_{12}H_{10}$	0.999
173.	1-Chlorododecane	204	$C_{12}H_{25}Cl$	1.000
174.	2,7-Dimethyltetrahydro-naphthalene	160	$C_{12}H_{16}$	1.000
175.	Pentachloropyridine	249	C_5NCl_5	1.015
176.	2,4-Dinitrotoluene	182	$C_7H_6O_4N_2$	1.021
177.	Pentachlorobenzene	248	C_6HCl_5	1.031
178.	2,4,5-Trichloroaniline	195	C_6H_4NCl	1.041
179.	2,3,4-Trichloroaniline	195	$C_6H_4NCl_3$	1.064
180.	2,3,5-Trimethylnaphthalene	170	$C_{13}H_{14}$	1.067
181.	Fluorene	166	$C_{13}H_{10}$	1.077
182.	Diethyl phthalate	222	$C_{12}H_{14}O_4$	1.079
183.	n-Nonylbenzene	204	$C_{15}H_{24}$	1.079
184.	4-Chlorophenyl phenyl ether	204	$C_{12}H_9OCl$	1.084
185.	1,2-Diphenylhydrazine	184	$C_{12}H_{12}N_2$	1.104
186.	2,4,5,6-Tetrachloro-m-xylene	242	$C_8H_6Cl_4$	1.111
187.	3,4,5-Trichloroaniline	195	$C_6H_4NCl_3$	1.128
188.	BHC isomer	288	$C_6H_6Cl_6$	1.153
189.	n-Decylbenzene	218	$C_{16}H_{26}$	1.158
190.	Hexachlorobenzene	282	C_6Cl_6	1.176
191.	Lindane	288	$C_6H_6Cl_6$	1.180
192.	BHC isomer	288	$C_6H_6Cl_6$	1.197
193.	Phenanthrene	178	$C_{14}H_{10}$	1.221
194.	a,a,a,a',a',a'-Hexachloro-p-xylene	310	$C_8H_4Cl_6$	1.223
195.	Anthracene	178	$C_{14}H_{10}$	1.228
196.	2,4,5-Trichlorobiphenyl	256	$C_{12}H_7Cl_3$	1.268
197.	1-Chlorohexadecane	160	$C_{16}H_{33}Cl$	1.301
198.	Heptachlor	370	$C_{10}H_5Cl_7$	1.309
199.	Aldrin	362	$C_{12}H_8Cl_6$	1.355
200.	2,3',4,5'-Tetrachlorobiphenyl	290	$C_{12}H_6Cl_4$	1.370

Table 9. Organics Detected in GAC-Inf. Sample by More Than One Analytical Method

	GAC-Inf. Contactor D				GAC-Inf. Contactor A	
	Bellar[a] P&T (ug/l)	Grob[b] CLSA (ng/l)	B L L E Neutrals (RS[d])	Acids (RS)	X A D - E E E Neutrals (RS)	Acids (RS)
Chloroform	56	10 ug/l				
1,1,1-Trichloroethane	400	8				
Trichloroethene	TD[e]	57				
Bromoform	0.2	.51 ug/l	75		8	
2-Ethyl-4-methyl-1,3-dioxolane		5 RAU[c]	25			
Bromodichloromethane	18	16 ug/l	420			
Chlorobenzene		14	9			
1,3,5-Trimethylbenzene		0 RAU	5			
1,2,4-Trimethylbenzene		3	5			
Dibromochloromethane	5.8	6.2 ug/l	229		14	
1,3-Dichlorobenzene		5	3	2		
Hexachloroethane		8	9			
1,2-Dichlorobenzene		17	19		60	
Tetrahydronaphthalene		40	49			
Naphthalene		NQ	8		11	
Phenylether		14 RAU	37			

Table 9. Continued

	GAC-Inf. Contactor D				GAC-Inf. Contactor A	
	Bellar P&T (ug/l)	Grob CLSA (ng/l)	B L L E Neutrals (RS)	B L L E Acids (RS)	X A D - E E E Neutrals (RS)	X A D - E E E Acids (RS)
Benzoic acid				102		200
Phenylpropanoic acid				2		4
m-Toluic acid				1.5		3
Phenylacetic acid				2.5		13
Dimethylmaleic acid				24		22
Ethylmethylmaleic acid				55		96
Hydrocinnamic acid				3.5		7
4-Methyl-2-acetylbenzoic acid				3.5		5
Anisic acid				3		8
Clofibric acid				10		9
Phthalic acid				1.5		8
2,4-Dichlorophenoxyacetic acid				3		5
Methylpropylbenzene isomer		3 RAU			2	
5-Ethyl-1,3-dimethylbenzene		0			3	
2-Ethyl-1,4-dimethylbenzene		2			2	
4-Ethyl-1,3-dimethylbenzene		NQ			2	
4-Ethyl-1,2-dimethylbenzene		1			4	
Benzonitrile			16		2	

Table 9. Continued

	GAC-Inf. Contactor D				GAC-Inf. Contactor A	
	Bellar P&T (ug/l)	Grob CLSA (ng/l)	B L L E Neutrals (RS)	B L L E Acids (RS)	X A D - E E E Neutrals (RS)	X A D - E E E Acids (RS)
o-Nitrotoluene			18		7	
2,4-Dinitrotoluene			7		8	

[a] Standards were obtained and quantitation is based upon an experimental response factor.

[b] Standards were obtained and quantitation is based upon an experimental relative response factor to that of chlorododecane, IS.

[c] $\text{RAU (Relative Area Unit)} = \frac{\text{Total Ion Current Area(UNK)}}{\text{Total Ion Current Area(IS)}} \times 52$

where: UNK = Unknown Compound
IS = Chlorododecane

[d] RS = Relative Size; GC/MS peak height compared to that of hexaethylbenzene, IS, 0.2 ppb.

[e] TD = Trace detected.

Table 10. Comparison[a] of Analysis Results of Four Methods Using Organic Functional Groups and EPA Lists of Toxic Compounds

I. Broad Categories	Bellar P &T		Grob CLSA		BLLE		XAD-EEE[b]	
	No.	%	No.	%	No.	%	No.	%
Aliphatic Hydrocarbon			26	24.3	6	6.7		
Aromatic Hydrocarbon			31	29.0	4	4.4	6	10.3
Halogenated Organic	6	100.0	26	24.3	16	17.8	10	17.2
Nitrogen Compound			1	0.9	8	8.9	6	10.3
Oxygen Compound			23	21.5	52	57.8	36	62.1
Sulfur Compound					1	1.1		
Phosphorous Compound					2	2.2		
Mercury Compound					1	1.1		
Total Compounds Detected	6	100.0	107	100.0	90	100.0	58	100.0
II. Specific Categories	**No.**	**%**	**No.**	**%**	**No.**	**%**	**No.**	**%**
Alkane			6	5.6				
Alkene, Alkyne			6	5.6	2	2.2		
Alicyclic Hydrocarbon			31	29.0	3	3.3	5	8.6
Benzene Hydrocarbon			7	6.5	1	1.1		
Indeno Hydrocarbon								
Biphenyl Hydrocarbon			4	3.7	1	1.1	1	1.7
Naphtheno Hydrocarbon					1	1.1		
Polyhydrofuran					1	1.1		
Aliphatic Mercury			3	2.8	2	2.2		
Polyhydronaphthalene					5	5.6	1	1.7
Alcohols					5	5.6		
Glycols								
Amines								
Phenols			6	5.6			1	1.7
Aldehydes			2	1.9	5	5.6		
Ketones			2	1.9				
Quinones			2	1.9			3	5.2
Aliphatic Esters			4	3.7	1	1.1	4	6.9
Aromatic Esters			3	2.8	1	1.1	2	3.4
Ethers					1	1.1		
Halogenated Ethers			1	1.0	15	16.7	16	27.6
Aliphatic Carboxylic Acids					18	20.0	15	25.9
Aromatic Carboxylic Acids							1	1.7
Amides					2	2.2	1	1.7
Nitriles			3	2.8	2	2.2		
Cyclic Oxygen			1	1.0	2	2.2	1	1.7
Basic Nitrogen							4	6.9
Aromatic Nitro								

Table 10. Continued

	Bellar P&T		Grob CLSA		BLLE		XAD-EEE[b]	
	No.	%	No.	%	No.	%	No.	%
Thiophenes								
Halogenated Aliphatic	6	100.0	15	14.0	10	11.1	2	3.4
Halogenated Aromatic			7	6.5	4	4.4	1	1.7
Halogenated Ketones			4	3.7				
Halogenated Phenols					1	.1.1		
Halogenated Amides								
Halogenated PCB & Pesticides								
Phosphates					2	2.2		
Total Number of Organics Detected	6	100.0	107	100.0	90	100.0	58	100.0
III. Total Number of Unique Organics Analyzed by All Four Methods was 183.								
Percent of Total Number of Unique Organics (183 organics)		3%		58%		49%		32%
IV. Total Number of Consent Decree Organics[28] (113 organics)	6		23		11		6	
Percent of Consent Decree Organics (113 organics)		5%		20%		10%		5%
V. Total Number of EPA Chemical Indicators in Drinking Water of Industrial Pollution[34] (62 organics)	2		18		10		5	
Percent of EPA Chemical Indicators in Drinking Water of Industrial Pollution (62 organics)		3%		29%		16%		8%

[a] Comparison is based upon GAC-Inf. water from Contactor D.
[b] XAD-Inf. water from Contactor A was used.

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